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

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

Improved methods have been developed for generating aliphatic ketyl radical anions in solution for study by EPR spectroscopy. These methods involve either photolysis of a solution of potassium in the corresponding alcohol (which probably proceeds by initial electron transfer to the solvent), or abstraction of a hydrogen atom from the corresponding alcohol by photolytically generated *tert*-butoxyl radicals under strongly basic conditions. The EPR spectra of a number of new aldehyde and ketone radical ions are described, and compared with the spectra of their conjugate acids. The value of $a(^{13}C\text{-}\alpha)$ in the acetone radical anion is found to be 52.2 G confirming that it is non-planar. The Arrhenius parameters for the inversion of the ring in the cyclohexanone radical anion are E_a = 6.6 kcal mol^{-1},† and log (A/s^{-1}) = 13.2.

Aromatic ketyl radical anions **1** (R = aryl) have been known for more than 100 years. They are readily prepared by electron transfer from an alkali metal [eqn. (1)], and they have been extensively investigated by EPR spectroscopy.[1]

$$\underset{\textbf{1}}{R_2C{=}O + M \longrightarrow R_2C{=}O^{\bullet -}M^+} \qquad (1)$$

The alkyl ketyl radical anions **1** (R = alkyl) are less familiar because aliphatic ketones and aldehydes in solution usually react with alkali metals with loss of a proton to give enolate ions, and attempts to generate **1** by this procedure have led to the erroneous identification of semidione radicals anions as being ketyl radical anions.[2]

However, the ketyl radical anions **1** are the conjugate bases of the hydroxyalkyl radicals **3**, and they can alternatively be prepared by sequential removal of a hydrogen atom and a proton from the corresponding alcohol **2** [eqn. (2)].

$$\underset{\textbf{2}}{R_2CHOH} \xrightarrow{HO^{\bullet}} \underset{\textbf{3}}{R_2\dot{C}OH} \xrightarrow{HO^{-}} \underset{\textbf{1}}{R_2C{=}O^{\bullet -}} \qquad (2)$$

The pK_a values of the hydroxyalkyl radicals **3** are substantially lower than those of the parent alcohols **2**,[3] and in aqueous solution at *ca.* pH 13, most hydroxyalkyl radicals are largely deprotonated.[4] Neta, Hoffmann and Simic[5] showed that if NO-saturated aqueous alkaline solutions of benzylic alcohols were irradiated with 2.8 MeV electrons, the EPR spectra of the corresponding benzaldehyde radical anions could be observed. Under these conditions, the reagents which abstract $H^{\bullet}$ and H^+ are $HO^{\bullet}$ and HO^-, respectively. Similarly Dobbs, Gilbert and Norman[4] made use of this principle to observe the EPR spectra of the ketyls $H_2C{=}O^{\bullet -}$, $MeHC{=}O^{\bullet -}$ and $Me_2C{=}O^{\bullet -}$ by a flow technique in which aqueous solutions of titanium(II) chloride, tartaric acid and sodium or potassium hydroxide, and of hydrogen peroxide and the appropriate alcohol (20 cm^3 dm^{-3}) were allowed to react as they flowed through the cavity at a rate of *ca.* 180 cm^3 min^{-1}; again the reactive species are $HO^{\bullet}$ and HO^-.

We have been interested in the principle under which a radical anion can be regarded as a deprotonated neutral radical[6,7] (and a cation as a protonated neutral radical)[8] and we wished to exploit this principle in the preparation of new radical anions, not only of carbonyl compounds but also of other multiply-bonded molecules such as thioketones ($R_2C{=}S^{\bullet -}$) and silanones ($R_2Si{=}O^{\bullet -}$)[9] where the corresponding multiply-bonded parent molecules might not be available. The necessary conditions were that special techniques such as pulse radiolysis[3] should not be required, that the method should be applicable to non-aqueous solutions at variable temperature, and should need relatively small amounts of reagents.

We report here four technical variants which fulfil these conditions. They involve the photolysis of potassium or sodium alkoxides in alcohols or of di-*tert*-butyl peroxide in the presence of potassium alkoxides and have provided spectra of good quality for a number of new radical anions.

Results and Discussion

Method A.—Photolysis of solutions of potassium alkoxides in the corresponding alcohols. Brand, Roberts and Strube[10] showed that when a solution of sodium 2-methylpropoxide in a mixture of liquid ammonia and 2-methylpropanol was irradiated with UV light, the EPR spectrum of the 2-methylpropanal radical anion could be observed with a[1(α-H)] 12.0, a[1(β-H)] 21.3 G, g 2.0035.

We find that UV photolysis of aliphatic primary or secondary alcohols containing the corresponding potassium alkoxides (*ca.* 0.1 mol dm^{-3}) gives strong spectra of the corresponding ketyl radical anions [eqn. (3), R = alkyl or H].

$$R_2CHO^-K^+ \xrightarrow[h\nu]{R_2CHOH} \underset{\textbf{1}}{R_2C{=}C^{\bullet -}} \qquad (3)$$

In polar solvents, anions with low ionisation energies show red-shifted absorption bands resulting from charge transfer to the solvent, and irradiation into these bands can induce electron transfer to the solvent.[11,12] We assume, as did Roberts *et al.*,[10] that the photolysis of solutions of sodium or potassium alkoxides in alcohols gives initially the corresponding alkoxyl radical and the solvated electron [eqn. (4)]. The electrophilic

$$R_2CH{-}O^- \xrightarrow{h\nu} R_2CHO^{\bullet} + e^-_{\text{solv}} \qquad (4)$$

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† 1 cal = 4.18 J.

alkoxyl radical then abstracts hydrogen from the alkoxide anion to give the ketyl radical anion [eqn. (5)]. As an example,

$$R_2CHO^{\bullet} + R_2CHO^{-} \longrightarrow R_2CHOH + R_2C{=}O^{\bullet -} \quad (5)$$

the spectrum of the radical anion of acetone which is obtained under these conditions is shown in Fig. 1, and from it the value of $a(^{13}C)$ can be measured for the first time to be 52.2 G.

The hyperfine coupling constants (hfcc) of the radical anions **1** are rather less than those of their corresponding conjugate acids, the 1-hydroxyalkyl radicals **3** (Tables 1 and 2) which are formed on photolysis of a solution of di-*tert*-butyl peroxide in the appropriate alcohol [eqn. (6)]. They are also slightly smaller

$$Bu^tO^{\bullet} + R_2CHOH \longrightarrow Bu^tOH + \underset{\mathbf{3}}{R_2\dot{C}OH} \quad (6)$$

than the values which have been reported previously for some examples of **1** in aqueous solution. This may reflect the effect of change of solvent, as the radical anions would be expected to be strongly solvated, but it might also be that the radical anions **1** are in equilibrium with the neutral radicals **3**. The latter explanation seems to be unlikely; in Fig. 2, the value for a(β-H) for the acetone radical ion prepared by reaction (3) is plotted against the concentration of the potassium alkoxide, and it shows that a reaches a minimum value at *ca.* 0.06 mol dm^{-3} potassium alkoxide, which is below the concentration at which we usually worked.

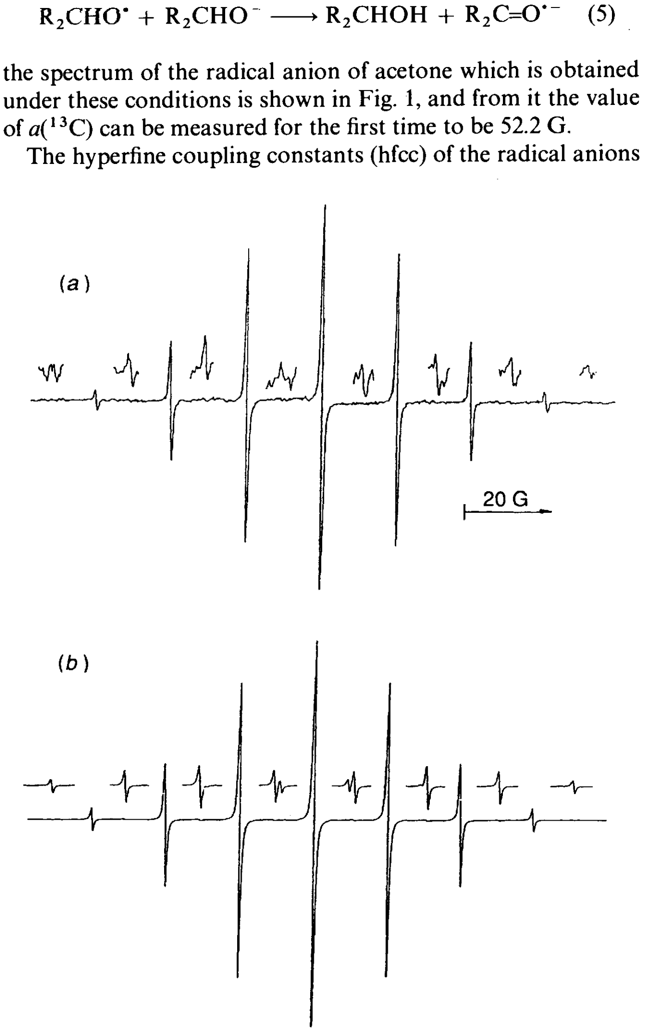


Fig. 1 (*a*) EPR spectrum of the acetone radical anion obtained from the photolysis of potassium isopropoxide in isopropyl alcohol at 300 K (method A). The ^{13}C satellites are shown at increased gain. (*b*) Computer simulation.

Method B.—Photolysis of solutions of potassium alkoxides in tertiary alcohols. In this second method, *tert*-butyl alcohol (m.p. 25 °C) or *tert*-pentyl alcohol (2-methylbutan-2-ol, m.p. −12 °C) was used as the bulk solvent; the latter was preferred because it allowed experiments to be carried out at a lower temperature, and the results quoted in Tables 1 and 2 refer to this solvent. This method has three advantages: it provides a constant solvent so that results with different alkoxides can be compared; it makes it

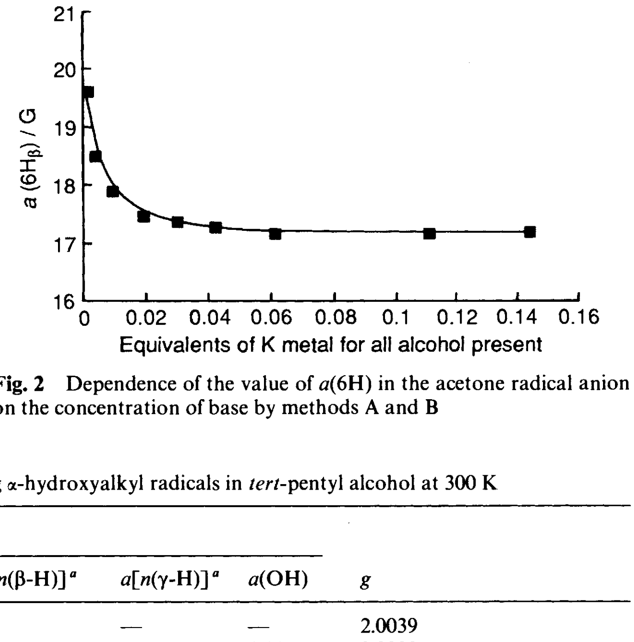


Fig. 2 Dependence of the value of a(6H) in the acetone radical anion on the concentration of base by methods A and B

Table 1 EPR parameters for aldehyde radical anions and the corresponding α-hydroxyalkyl radicals in *tert*-pentyl alcohol at 300 K

		hfccs				
Radical	Method	$a[n(\alpha\text{-H})]$[a]	$a[n(\beta\text{-H})]$[a]	$a[n(\gamma\text{-H})]$[a]	a(OH)	g
$H_2C{=}O^{\bullet -}$	D	14.02 (2)	—	—	—	2.0039
$H_2\dot{C}OH$		17.27 (2)	—	—	1.11	2.0033
$MeHC{=}O^{\bullet -}$	D	12.05 (1)	19.85 (3)	—	—	2.0036
$MeH\dot{C}OH$		15.24 (1)	22.11 (3)	—	0.27	2.0030
$EtHC{=}O^{\bullet -}$	D	11.72 (1)	20.99 (2)	0.40 (3)	—	2.0036
$EtH\dot{C}OH$		14.94 (1)	21.14 (2)	0.32 (3)	*b*	2.0032
$Pr^iHC{=}O^{\bullet -}$	D	10.92 (1)	19.31 (1)	—	—	2.0036
$Pr^iH\dot{C}OH$		14.47 (1)	21.39 (1)	—	*b*	2.0032
$Bu^tHC{=}O^{\bullet -}$	B	8.65 (1)	—	0.29 (9)	—	2.0036
$Bu^tH\dot{C}OH$		13.78 (1)	—	0.33 (9)	*b*	2.0030
		$a[n(1\text{-H})]$			a(2-H)	
$H_2C{=}CH{-}HC{=}O^{\bullet -}$	B	13.17, 12.26, 10.32, 2.21 (4)			—	2.0035[c]
$H_2C{=}CH{-}HCOH$	B	14.22, 3.47, 0.68 (3)			12.94	2.0031[d]
		13.24, 3.03, 0.58 (3)			13.74	2.0030[d]

[a] The value of *n* is shown in parentheses after the coupling. [b] No coupling by the OH proton could be seen at 300 K, but at lower temperatures this coupling was resolved. [c] Only one radical was observed, and this was assumed to have the s-*trans* structure. [d] Two radicals were observed; the one with the more intense spectrum was assumed to have the s-*trans* structure.

Table 2 EPR parameters for ketone radical anions and the corresponding α-hydroxyalkyl radicals at 300 K

Radical	Method	hfccs $a[n(\beta\text{-H})^a$	$a[n(\beta'\text{-H})^a$	$a[n(\gamma\text{-H})^a$	$a(\text{OH})$	g
$Me_2\underset{\bullet}{C}{=}O^{\bullet -}$	B	16.90 (6)	—	—	—	2.0036
$Me_2\dot{C}OH$		19.62 (6)	—	—	—	2.0031
$MeEt\underset{\bullet}{C}{=}O^{\bullet -}$	B	16.91 (3)	15.56 (2)	0.42 (3)	0.46 (^{23}Na)^b	2.0034
$MeEt\dot{C}OH$		19.60 (3)	17.11 (2)	0.35 (3)	0.35	2.0031
$Et_2\underset{\bullet}{C}{=}O^{\bullet -}$	B	14.30 (4)	—	0.42 (6)	0.46 (^{23}Na)^b	2.0034
$Et_2\dot{C}OH$		16.75 (4)	—	—	—	2.0031
cyclo-$C_4H_8\underset{\bullet}{C}{=}O^{\bullet -}$	B	26.3 (4)	—	—	—	2.0031
cyclo-$C_4H_8\dot{C}OH$		28.0 (4)	—	0.32 (4)	0.32	2.0038
cyclo-$C_5H_{10}\underset{\bullet}{C}{=}O^{\bullet -}$	B	32.9 (2)	8.4 (2)	—	—	2.0032
cyclo-$C_5H_{10}\dot{C}OH$		35.5 (2)	10.1 (2)	—	—	2.0032

[a] The value of *n* is shown in parentheses after the coupling. [b] Sodium *tert*-butoxide was used as the base.

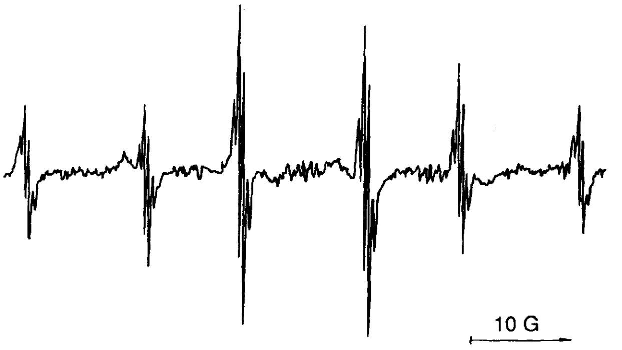


Fig. 3 EPR spectrum of the propanal radical anion in *tert*-pentanol obtained by method B

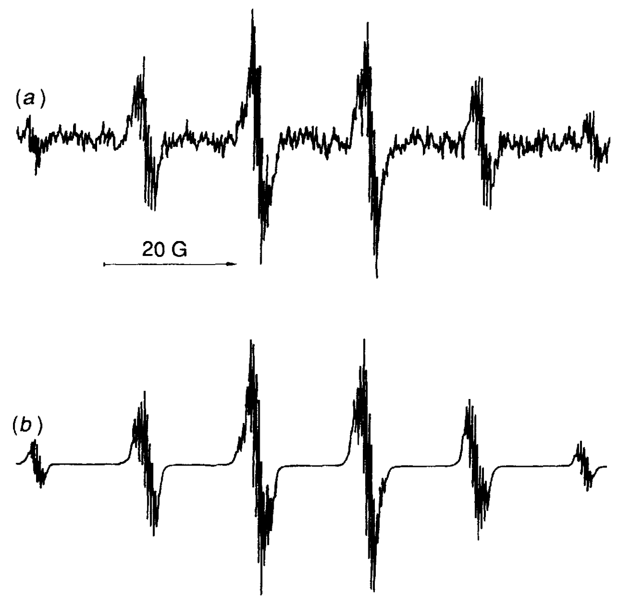


Fig. 4 (*a*) EPR spectrum of the butan-2-one radical anion at 300 K in *tert*-butyl alcohol, prepared by method B, and showing ^{23}Na hyperfine coupling. (*b*) Computer simulation.

possible to study alkoxides derived from solid alcohols; and, because of the higher basicity of the medium, it reduces the danger that the protic radical **3** might not be fully dissociated.

This technique gave significantly stronger spectra than those obtained by method A, but the hfcc values were slightly lower when the tertiary alcohol was present. If sodium rather than potassium alkoxide was used as the base, hyperfine coupling to the ^{23}Na counter cation could be detected (see Table 2). Typical spectra are shown in Figs. 3 and 4. Care was taken to work always at a base concentration in the region where the hfcc had reached its minimum value (Fig. 2).

The acetone radical anion in aqueous solution at pH 13.2 shows a(6H) 17.2 G. Norman pointed out[4] that at this pH the hydroxyalkyl radical is only 91% dissociated, and that a(6H) would be 16.9 G if dissociation were complete. For comparison, the value we observe in tertiary alcohol solvent is indeed 16.9 G, but the coincidence is probably accidental as there is likely to be a significant solvent effect on the coupling constant because of hydrogen bonding.

This method gave good results with a large range of primary and secondary alcohols, but it was not without its problems. Occasionally a sample which normally worked well would give no signal or one which developed slowly on photolysis after an induction period of *ca.* 1 min. This was not caused by the presence of molecular oxygen through incomplete degassing, because samples saturated with oxygen gave normal results (and on occasion, no signal at all). We are not able to account for this erratic behaviour.

More significantly, no spectrum at all could be obtained by this technique for some alcohols; in particular, although isopropyl alcohol and cyclopentanol gave good spectra, no spectrum could be obtained for the structurally related cyclohexanol.

*Method C.—Photolysis of a static solution of di-*tert*-butyl peroxide and potassium alkoxide.* In this method potassium was dissolved in a dilute solution of the primary or secondary alcohol in *tert*-pentyl alcohol; di-*tert*-butyl peroxide was then added and the sample was photolysed in the cavity with UV light. As the tertiary alcohol is the weakest acid, most of the primary or secondary alcohol will be present as the alkoxide, and the principal reactions which occur are probably those shown in eqns. (7) and (8). If any undissociated primary or secondary alcohol is present, and reaction (6) occurs, the α-hydroxyalkyl radical **3** which is formed will rapidly deprotonate to give the ketyl radical anion, and similarly if any of reaction (3) occurs, it will give the same radical anion.

$$Bu^tO{-}OBu^t \xrightarrow{h\nu} 2Bu^tO^{\bullet} \qquad (7)$$

$$Bu^tO^{\bullet} + R_2CH{-}O^- \longrightarrow Bu^tOH + R_2C{=}O^{\bullet -} \qquad (8)$$

Photolysis with UV light, either unfiltered or filtered through Pyrex glass, gave EPR spectra of the appropriate ketyl radical anions which were stronger than those obtained in the absence of the peroxide (method B). The hfcc values were similar to those observed with methods A and B if allowance is made for the change of solvent. The spectra were stronger with unfiltered light, as would be expected as the peroxide has only a weak absorption above 325 nm.

However, these strong signals quickly decayed, and it was difficult to record good spectra as the intensity decreased five- or ten-fold during a 4 min scan. The solutions had acquired an obvious yellow or orange colour with a maximum at 280 nm and an absorbance *ca.* 11 times that of di-*tert*-butyl peroxide. The decay of the signal therefore probably results from preferential absorption of the light by this coloured compound, which prevents the dissociation of the peroxide.

The following observations concerning the generation of this coloured compound were made.

(*a*) If either the di-*tert*-butyl peroxide, or the substrate alcohol, or the base were omitted, the compound was not formed.

(*b*) The solutions showed a negative test with 2,4-dinitrophenylhydrazine for aldehydes or ketones before photolysis, but a positive test after photolysis. Solutions prepared according to (*a*) showed no such result.

(*c*) Addition of the aldehyde or ketone corresponding to the primary or secondary alcohol to the basic solutions, or to *tert*-butyl alcohol containing potassium *tert*-butoxide, gave rise to a coloured compound with a similar absorption spectrum at a similar rate. If the base was omitted from the solutions, no colour was formed. The rate of development of the colour increased as the base concentration increased.

(*d*) The EPR spectrum decayed more quickly if the concentration of the di-*tert*-butyl peroxide was increased.

(*e*) No colouration and no decay of the EPR spectrum was observed when the substrate alcohol was methanol or 2,2-dimethylpropan-1-ol.

These observations are consistent with the colour being due to the progressive aldol condensation then dehydration of the aldehydes or ketones corresponding to the primary or secondary alcohols (*e.g.* acetone forming isophorone). With methanol or 2,2-dimethylpropanol, the absence of a β-proton in the corresponding carbonyl compounds (methanal or 2,2-dimethylpropanal) precludes any aldol condensation.

Di-*tert*-butyl peroxide has to be present in the sample for the colour to be formed, and we conclude that the peroxide (reduction potential *ca.* −0.96 V) oxidises the ketyl radical anion (reduction potential *ca.* −2.5 V) to aldehyde or ketone [eqn. (9)]. A corollary of this is that the normal route of decay

$$R_2C{=}O^{\cdot -} + Bu^tOOBu^t \longrightarrow R_2C{=}O + Bu^tOOBu^{t\cdot -} \qquad (9)$$

of the ketyl radicals in the absence of the peroxide is not to give the corresponding aldehydes or ketones. Neta[13] and Fischer[14] have shown that in aqueous solution the decay of the acetone radical anion is cleanly second-order with a rate constant at room temperature of *ca.* 0.3×10^9 dm^3 mol^{-1} s^{-1}, presumably giving the corresponding pinacol.

Dissociation of the peroxide radical anion [eqn. (10)] could

$$Bu^tOOBu^{t\cdot -} \longrightarrow Bu^tO^{\cdot} + Bu^tO^- \qquad (10)$$

then set up a chain reaction which could further reduce the lifetime of the sample. By working with low concentrations of the base and peroxide, the rate of loss of signal intensity could be reduced so that spectra of reasonable quality could be obtained, but the lifetime of the samples was still unacceptably short.

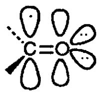
*Method D.—Photolysis of a flowing solution of di-*tert*-butyl peroxide and potassium alkoxide.* To overcome the problem of the build up of carbonyl condensation products which absorbed the light and of the possible intervention of the chain-carrying reaction (10), the solutions were slowly flowed through the cavity at a rate of 0.3–0.8 cm^3 min^{-1} so as to sweep contaminated material from the cell. The more rapid rates of flow gave the stronger spectra, but even at the slowest rates this technique gave the strongest signals and worked most consistently. Cyclopentane could be added to provide a useful increase in sample volume without usually affecting the signal strength or the hfcc values or *g* value, but sometimes it gave rise to weak signals of the cyclopentyl radical, and its use is not recommended for obtaining high quality spectra.

Good spectra of the cyclopentanone radical anion could be obtained by methods A or B, but this spectrum was swamped by those of other radicals when methods C or D were used. If our picture of the mechanism of the reaction in methods A and B is correct, this suggests that the *tert*-butoxyl radical is less regioselective than the cyclopentyloxyl radical in abstracting hydrogen. On the other hand we could observe the formation of the cyclohexanone radical anion only by methods C and D, and not by methods A and B.

The hfcc values and *g* values of the 11 ketyl radical anions **1** which have been observed by methods B or D, and the neutral hydroxymethyl radicals **3** which have been prepared by reaction (6), are collected in Tables 1 and 2. Seven of the ketyl radical anions have not been observed previously in fluid solution.

The only ketone with which we could not obtain a satisfactory spectrum under any conditions was diisopropyl ketone. Possible reasons for this failure might be steric hindrance, and the presence of the two isopropyl groups which themselves would be susceptible to hydrogen abstraction by an alkoxyl radical.

Overview of Spectra.—In both the ketyl radical ions **1** and the α-hydroxyalkyl radicals **3**, the unpaired electron occupies an antibonding π* orbital; the principal difference between the two species is that **1** has two non-bonding electron pairs in the nodal plane of the π system as illustrated in **4**, whereas in **3** one of these pairs is shared with a proton as shown in **5**. It is not surprising therefore that the unpaired electron should be similarly distributed in the two species, and that they should show similar EPR spectra.



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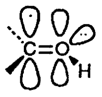

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For 13 of the 15 values of *a*(α-H) and *a*(β-H) listed in Tables 1 and 2, the ratio between the values for the radical anions **1** and their conjugate acids **3** lies within the limits of 0.76 and 0.94. The two values which lie outside this range are *a*(α-H) (0.64) for the pair $Bu^tHC{=}O^{\cdot -}/Bu^tH\dot{C}{-}OH$, and *a*(β-H) (0.99) for the pair $EtHC{=}O^{\cdot -}/EtH\dot{C}{-}OH$.

These ^1H hfcc values will be determined by the spin density on C-α and on any change in hybridization at C-α. Intermediate neglect of differential overlap (INDO) calculations on the MNDO optimised geometry of the acetone radical anion $Me_2C{=}O^{\cdot -}$ give the electron densities at C-α and at O to be 0.75 and 0.2, respectively, whereas for the conjugate acid $Me_2\dot{C}OH$ the corresponding values are 0.85 and 0.11. The ratio in spin densities at C-α are calculated to be 0.88, in line with what we observe (although of course these calculations refer to isolated molecules in the gas phase, and do not take into account any solvent or counter-ion effects). It seems likely then that the lower values in *a*(H) in the radical anion result principally from a lower spin density at C-α.

The Formaldehyde Radical Anion.—In *tert*-butyl alcohol, the formaldehyde radical anion shows a triplet spectrum with *a*[2(α-H)] 14.0 G. A value of 14.4 G has been observed before for the radical anion in aqueous solution. Norman[4] has calculated that under these conditions deprotonation of the

Table 3 Temperature dependence of $a[2(\alpha\text{-H})]$ in the hydroxymethyl radical and the formaldehyde radical anion

	$a[2(\alpha\text{-H})]$/G	
T/K	$H_2\dot{C}OH$	$H_2C{=}O^{\bullet-}$
300	17.27	14.03
275	17.37	14.19
250	17.53	14.39
225	17.69	14.58
200	17.82	14.85

Table 4 Values of $a(^{13}C)$ in the acetone radical anion and related molecules

Radical	$a(^{13}C\text{-}\alpha)$/G	Ref.
$H_3C^\bullet$	38.3	*a*
$H_2C{=}O^{\bullet-}$	37.7	*b*
$Me_2CH^\bullet$	41.3	*c*
$Me_2C{=}O^{\bullet-}$	52.2	*d*
$Me_2\dot{C}OH$	65.0	*e*
$Bu^t_2C{=}O^{\bullet-}$	52.7	*f*

[a] R. W. Fessenden, *J. Chem. Phys.*, 1967, 71, 74. [b] G. P. Laroff and R. W. Fessenden, *J. Chem. Phys.*, 1972, **57**, 5614. [c] H. Paul and H. Fischer, *Helv. Chim. Acta*, 1973, **56**, 1575. [d] This work. [e] A. J. Dobbs, B. C. Gilbert and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1972, 786.

neutral radical **3** is 99% complete. The significant difference between these two values is therefore probably due to a solvent effect.

The line width of this radical ion (*ca.* 1.2 G) is much larger than for the other ketyl radical anions which we have observed (*e.g.* $Me_2C{=}O^{\bullet-}$, *ca.* 0.2 G), and as the temperature is reduced, the lines broaden further unsymmetrically, the hyperfine coupling increases, and the *g* value increases. This is consistent with a shift in the equilibrium of eqn. (11) to the left, the

$$H_2\dot{C}\text{–}OH \overset{-H^+}{\rightleftharpoons} H_2C{=}O^{\bullet-} \qquad (11)$$

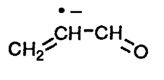
unsymmetrical broadening being caused by the fact that the radical ion and the neutral radical have different *g* values so that the three lines undergo different frequency shifts. Under these conditions, the observed *g* value is the concentration-weighted average of the individual *g* values, and as these are known the relative concentrations of the formaldehyde radical anion and of the hydroxymethyl radical at various temperatures can be calculated. From this, and a knowledge of $a[2(\alpha\text{-H})]$ for the neutral radical, the value for $a[2(\alpha\text{-H})]$ in the radical anion can be calculated. The results are shown in Table 3, which shows that the temperature dependence of the radical anion is rather greater than that of the neutral radical.

The Acetone Radical Anion.—The most intense spectrum observed in this study was that of the acetone radical anion (Fig. 1) which was obtained by photolysis of a solution of potassium isopropoxide in isopropyl alcohol, and from which $a(^{13}C\text{-}\alpha)$ could be obtained. Values of $a(^{13}C\text{-}\alpha)$ in related molecules are collected in Table 4.

The most significant point is the comparison between the values in $Me_2CH^\bullet$ and $Me_2C{=}O^{\bullet-}$. The value of $a(^{13}C\text{-}\alpha)$ will depend on the electron density at the carbon and on the degree of bending which will confer some s orbital character on the singly-occupied orbital at carbon; any spin polarization contribution to $a(^{13}C\text{-}\alpha)$ by the spin density on oxygen would be expected to be negative in sign and reduce the observed value.[15,16] Although in the radical anion some of the unpaired electron is delocalised onto oxygen, the value of $a(^{13}C\text{-}\alpha)$ is greater than it is in the neutral radical. This must mean that the radical anion is more bent than the neutral radical. This is in accord with many calculations which have been carried out, mainly on the radical anion of formaldehyde. For example, *ab initio* calculations with a 4-31G basis set, which gives geometries for formaldehyde in good agreement with experimental data, suggest that in the radical anion the C=O bond is bent out of the plane containing the CH_2 group by 27.5°.[17,18]

It is interesting that the value[16] of $a(^{13}C)$ implies that the radical anion of di-*tert*-butyl ketone is apparently bent to the same degree, despite the steric hindrance which is involved. The formaldehyde radical anion on the other hand appears to be closer to planar. This would be in accord with the fact that increasing α-alkylation of an alkyl radical tends to distort it from a planar towards a pyramidal geometry.

The Propenal Radical Ions.—The EPR spectra of the s-*cis*- and s-*trans*-propenal radical anions have been observed before by the electron irradiation of an aqueous solution of propenal saturated with N_2O,[19] and by the flow technique using the Ti^{III}/H_2O_2 system and methyloxirane at pH 10.[20] Both conditions gave rise to two spectra with the relative intensities 1:1.5, which were assigned to the s-*cis*- and s-*trans* isomers (**6** and **7**), respectively.



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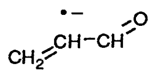

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By our method B (photolysis of a solution of the potassium salt of allyl alcohol in *tert*-pentyl alcohol) we obtained only one spectrum which we assume is to be ascribed to the radical anion of s-*trans*-propenal **7**. The small differences from the hfcc values which have been reported previously are probably due to the solvent effect. Methylation in the 2-position confirms that this is the site of the proton with the small hfcc but the necessary deuteriation experiments have not been carried out to permit the assignments of the three large coupling constants. Our rule relating the coupling constants between the ketyl radical anion and its conjugate base does not help because the assignments similarly are not known for the hydroxypropenyl radical. Clearly however the two isomers are not equilibrating under the conditions of our experiment.

The Cyclopentanone and Cyclohexanone Radical Anions.—This pair of ketones proved to be difficult to handle by any of our methods. Cyclopentanone gave good spectra of the radical anion by methods A and B, but by methods C and D this spectrum was swamped by other signals probably from radicals formed by reaction of *tert*-butoxyl radicals unselectively at the cyclopentyl ring. On the other hand spectra could be obtained from cyclohexanone only by methods C and D.

The cyclopentanone radical anion has been observed before using a rotating cryostat;[21] at 100 K the four β-hydrogen atoms appear as pseudo axial and equatorial pairs with hfcc values of *ca.* 33 and 23 G, but at 150 K the four protons became equivalent, with a coupling of *ca.* 28 G. At 300 K, our method B gave a spectrum consisting of a binomial quintet with $a[4(\beta\text{-H})]$ 26.3 G, and this pattern persisted to the lowest temperature at which the technique could be used.

Cyclohexanone did not give a satisfactory spectrum by any of our four standard techniques. Ultimately, good spectra were obtained by the photolysis of di-*tert*-butyl peroxide in neat cyclohexanol in which potassium had been dissolved. Even then the spectra could be obtained only between *ca.* 215 and 280 K. At the low end of this temperature range the spectrum appeared

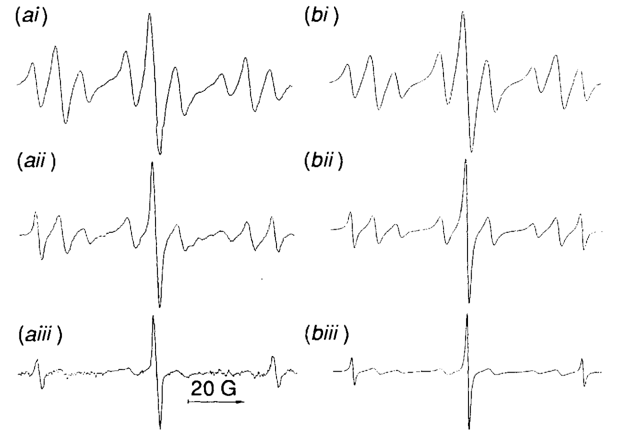


Fig. 5 EPR spectra of the cyclohexanone radical anion in *tert*-pentyl alcohol. (*ai*), (*aii*) and (*aiii*) show the observed spectra at 224, 240 and 255 K, respectively; and (*bi*), (*bii*) and (*biii*) show the simulated spectra for these temperatures with $a[2(\beta\text{-H})]$ 8.4 and $a[2(\beta'\text{-H})]$ 32.9 G, and exchange rates $k = 4.6 \times 10^6$, 1.5×10^7 and 3.3×10^7 s^{-1}, respectively.

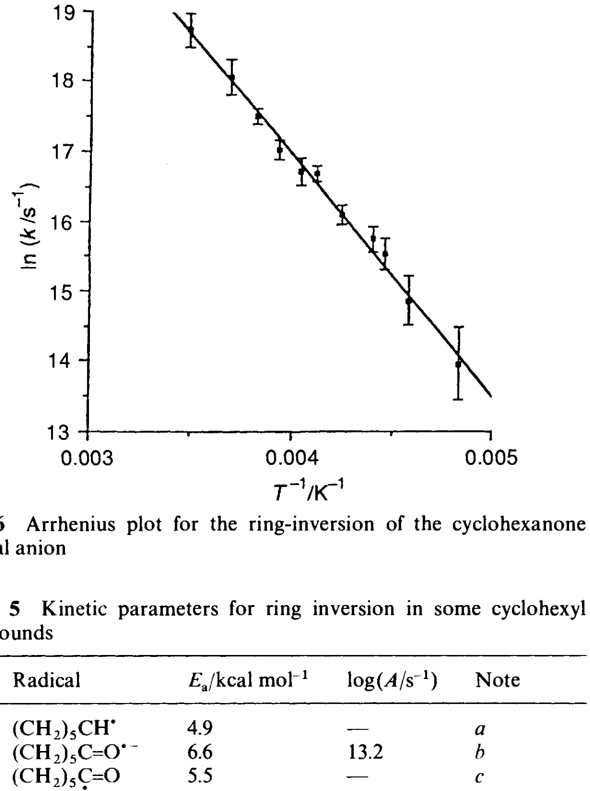


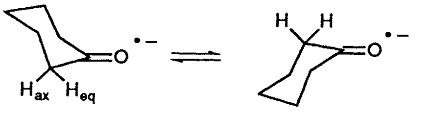
Fig. 6 Arrhenius plot for the ring-inversion of the cyclohexanone radical anion

Table 5 Kinetic parameters for ring inversion in some cyclohexyl compounds

Radical	E_a/kcal mol^{-1}	log(A/s^{-1})	Note
$(CH_2)_5CH^{\bullet}$	4.9	—	*a*
$(CH_2)_5C{=}O^{\bullet -}$	6.6	13.2	*b*
$(CH_2)_5\underset{\bullet}{C}{=}O$	5.5	—	*c*
$(CH_2)_5\dot{C}{-}OH$	6.6	13.7	*d*

[a] In the solid state between −85 and 0 °C; A. Ogawa and R. W. Fessenden, *J. Chem. Phys.*, 1964, **41**, 994. [b] Neat liquid. This work. [c] In the gas phase, by far IR spectroscopy; H. Wieser, T. L. Smithson, N. Ibrahim and P. J. Kreuger, *Can. J. Chem.*, 1983, **61**, 1924. [d] In cyclopropane solution; R. V. Lloyd and J. G. Causey, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1143.

as a triplet of triplets resulting from coupling to non-equivalent pairs of axial and equatorial protons (Fig. 5). As the temperature increased the rate of ring inversion [eqn. (12)] increased and the distinction between the two types of proton began to be lost. All the lines except those at the wings and the centre broadened and at 255 K the spectrum consisted of three lines of intensities *ca.* 1:4:1. The region of fast exchange where the spectrum should consist of a binomial quintet could not be studied because above 280 K signals from other radicals swamped the desired spectrum.



(12)

The best quality spectra were obtained when the sample was caused to flow slowly through the cavity, but under these conditions it was difficult to measure the sample temperature accurately because the solution did not have sufficient time to equilibrate. For kinetic measurements, the quality of the spectra was sacrificed in favour of an accurate knowledge of the temperature. Simulation of the spectra so obtained (Fig. 5) gave the rate constants illustrated in the Arrhenius plot in Fig. 6.

The Arrhenius parameters for some related cyclohexane derivatives are collected in Table 5. The activation barriers to inversion in the 1-hydroxycyclohexyl radical, and in cyclohexanone and its radical anion are seen to be similar within the probable error of *ca.* 0.5 kcal mol^{-1} and the uncertainty introduced by the change of phase, but they are significantly larger than the barrier in cyclohexane.

Experimental

Materials.—Di-*tert*-butyl peroxide was washed with aqueous silver nitrate, dried ($MgSO_4$), passed down a short column of basic aluminium oxide, and then fractionally distilled. *tert*-Butyl and *tert*-pentyl alcohols were distilled off their sodium salts, and cyclopentane was distilled off sodium then stored over sodium.

EPR Spectroscopy.—Spectra were recorded using a Varian E-109 instrument fitted with an Osram HBO-500 W/2 mercury discharge lamp in an Oriel Universal 1 kW housing. The light was focused on the cavity through a system of silica lenses, and an aqueous solution of nickel(II) sulfate (0.38 mol dm^{-3}), cobalt(II) sulfate (0.07 mol dm^{-3}) and sulfuric acid (0.04 mol dm^{-3}) to reduce heating of the sample. The temperature in the microwave cavity was controlled by a flow of pre-cooled nitrogen gas, and measured with a thermocouple calibrated against the value of $a(\beta\text{-H})$ of the isobutyl radical which was generated in the sample cell.

To prepare samples for methods A–D, the alcohol, mixed with *tert*-butyl or *tert*-pentyl alcohol if required, was allowed to react with cyclopentane-washed potassium (0.05–0.1 equivalents with respect to combined solute and solvent alcohols). Di-*tert*-butyl peroxide and pentane were added if required, and the mixture was then degassed in the sample tube with a stream of nitrogen for 5 min. If more rigorous degassing was required, the sample was subjected to three freeze–thaw cycles, and the tube was then sealed. Note that the peroxide must not be present when the potassium is added, because they react.

For method D, which required the sample to be flowed through the cavity, the solution was taken up into a 5 or 10 cm^3 syringe which was fitted in a syringe pump, and then passed *via* polyvinyl chloride tubing up through a nitrogen-flushed sample cell in the cavity. Flow rates of 0.5 cm^3 min^{-1} gave good spectra; faster flow rates gave better signal-to-noise ratios, but they were not used because they consumed too much sample.

The technique for generating the 1-hydroxyalkyl radicals was the same as that for method B, except that the potassium was omitted.

Acknowledgements

We thank the SERC for support.

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Paper 1/04341B
Received 20*th August* 1991
Accepted 10*th October* 1991