

Electron Spin Resonance Studies. Part XXXIV.¹ The Use of the *aci*-Anion from Nitromethane as a Spin Trap for Organic Radicals in Aqueous Solution

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The *aci*-anion $\text{CH}_2\text{:NO}_2^-$ has been used as a spin trap for a variety of organic radicals, which have been generated in aqueous solution by reactions effected by the hydroxyl radical or the sulphate radical anion, $\text{SO}_4^{\cdot-}$. The resulting species have been identified by their e.s.r. parameters, confirmation being obtained where necessary by independent generation of the species from the appropriate nitro-compound and a one-electron donor ($\cdot\text{CMe}_2\text{OH}$). Of especial value in the analysis, splitting is observed not only from the (β -) methylene protons in $\text{RCH}_2\text{NO}_2^{\cdot-}$ but also in almost all cases from γ -protons and, in some cases, from δ -protons; further, a_N and $a_H(\beta\text{-CH}_2)$ are significantly dependent upon structure. For radicals of the type $\text{CXYZ}\cdot\text{CH}_2\text{NO}_2^{\cdot-}$, the splittings of the two β -methylene protons are unequal, evidently as the result of the chirality of the neighbouring carbon atom. In some cases information has been obtained about the mechanisms of reaction, as in comparison of the reactions of $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$ with carboxylate ions and of those of 2-chloro- and 2-iodoethanol with $\cdot\text{OH}$.

THERE has been considerable success in the last decade in generating highly reactive organic radicals in solution at concentrations above the detectable limit for e.s.r. spectroscopy; the methods include electron-bombardment, developed by Fessenden and Schuler,² the use of inorganic redox systems [especially titanium(III) ion-hydrogen peroxide],³ and ultraviolet irradiation.^{4,5} However, some species can still defy detection; for example, there is evidence for the rapid formation of the phenyl radical by the one-electron reduction of benzenediazonium ion in aqueous solution by, for example, the radical $\cdot\text{CMe}_2\text{OH}$, but the e.s.r. spectrum of the phenyl radical cannot be observed.⁶ Moreover, there may be a need to test for the presence of a particular radical in a

reaction which yields radicals relatively slowly. In such circumstances, it is often beneficial to carry out the reaction in the presence of a 'spin trap'—a compound which reacts efficiently with short-lived radicals to give much longer lived radicals; thus, the latter species can build up to concentrations which are readily detectable by the e.s.r. method. Two widely used traps are 2-methyl-2-nitrosopropane and *N*-butylbenzylidene-nitrene; each normally reacts with radicals to give relatively stable, long-lived nitroxides. The relative merits of the two have been summarised,⁷ and both improvements (*e.g.* the use of the perdeuterio-analogue

⁴ R. Livingston and H. Zeldes, *J. Chem. Phys.*, 1966, **44**, 1245.

⁵ J. K. Kochi and P. J. Krusic, in 'Essays on Free-radical Chemistry,' *Chem. Soc. Special Publ.* **24**, 1970, ch. 7.

⁶ A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc. (B)*, 1969, 403.

⁷ E. G. Janzen, *Accounts Chem. Research*, 1971, **4**, 31; M. J. Perkins in 'Essays on Free-radical Chemistry,' *Chem. Soc. Special Publ.* **24**, 1970, ch. 5; C. Lagercrantz, *J. Phys. Chem.*, 1971, **75**, 3466.

¹ Part XXXIII, B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 794.

² R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.

³ R. O. C. Norman, in 'Essays on Free-radical Chemistry,' *Chem. Soc. Special Publ.* **24**, 1970, ch. 6.

of the former trap, to give narrower lines in the e.s.r. spectrum⁸) and modifications⁹ have been reported; and other traps have been used which include nitrite ion (successful for trapping the phenyl radical to give the much longer-lived radical anion,⁶ PhNO_2^-), fumarate ion,¹⁰ and aromatic nitrile *N*-oxides¹¹ (to give the moderately stable iminoxyl radicals). Possible ambiguities in the uses of such traps have been pointed out; thus, the formation of a nitroxide radical from a nitroso-compound or a nitrene does not necessarily indicate that a radical has added to the trap since nucleophiles also add rapidly to these reagents and the species which result are readily oxidised to nitroxides.¹²

The *aci*-anion from nitromethane, $\text{CH}_2\cdot\text{NO}_2^-$, has already been employed successfully in this laboratory as a trap for hydroxyl and aminyl radicals,¹³ substituted aminyl radicals,¹⁴ and the carbon dioxide radical-anion,¹⁵ and both here¹⁶ and elsewhere¹⁷ as a trap for sulphur-containing radicals. We now report on a study of its utility as a trap for carbon-centred radicals; one oxygen-centred radical has also been trapped. Particular attention has been given to trapping radicals of the type $\cdot\text{CXYZ}$ which yields species $\text{CXYZ}\cdot\text{CH}_2\text{NO}_2^-$ in which the methylene protons are magnetically inequivalent.

RESULTS AND DISCUSSION

Radicals were generated, with the rapid flow and mixing technique, by including the appropriate organic compound and nitromethane in either the titanium(III) ion-hydrogen peroxide system³ or the titanium(III) ion-persulphate system;¹⁸ reactions were carried out at pH 8–9.5, in the presence of a sequestering agent (usually ethylenediaminetetra-acetic acid) for titanium ions. The e.s.r. parameters for the resulting trapped radicals are in Tables 1 and 2; the assignments are justified in the sequel. The discussion does not follow the order of presentation of the radicals in the Tables, the former being based on the oxidant system employed and the type of compound oxidised and the latter on groupings of radicals of common structural type. Where two line-widths are quoted for a radical, the first (upper) refers to the outermost lines of the 1:2:1 triplet from interaction with equivalent β -protons (Table 1) or the 1:1:1:1 pattern from interaction with inequivalent β -protons (Table 2), and the second (lower) value refers to the corresponding inner line or lines, respectively.

⁸ R. J. Holman and M. J. Perkins, *J. Chem. Soc. (C)*, 1971, 2324.

⁹ See, e.g., S. Terabe and R. Konaka, *J. Amer. Chem. Soc.*, 1971, **93**, 4306; J. G. Pacifici and H. L. Browning, jun., *ibid.*, 1970, **92**, 5231.

¹⁰ P. Neta, *J. Phys. Chem.*, 1971, **75**, 2570.

¹¹ B. C. Gilbert, V. Malatesta, and R. O. C. Norman, *J. Amer. Chem. Soc.*, 1971, **93**, 3290.

¹² A. R. Forrester and S. P. Hepburn, *J. Chem. Soc. (C)*, 1971, 701.

¹³ D. J. Edge and R. O. C. Norman, *J. Chem. Soc. (B)*, 1969, 182.

¹⁴ N. H. Anderson and R. O. C. Norman, *J. Chem. Soc. (B)*, 1971, 993.

Titanium(III) Ion-Hydrogen Peroxide System.—(a) *Alcohols.* Each of the alcohols studied gave a spectrum showing the presence of a mixture of the nitromethane radical anion,¹⁹ presumably formed by reduction of nitromethane by an α -hydroxyalkyl radical,¹⁹ and one or more radicals formed by addition to the *aci*-anion $\text{CH}_2\cdot\text{NO}_2^-$; the proportion of the former species in the mixture varied from a trace to ca. 15%. Methanol, ethanol, and propan-2-ol gave the adducts (5), (21), and (6), respectively, by addition of the radicals $\cdot\text{CH}_2\cdot\text{OH}$, $\cdot\text{CHMe}\cdot\text{OH}$, and $\cdot\text{CMe}_2\cdot\text{OH}$; their spectra have been observed before,^{20,21} although no attention has previously been drawn to the line-width alternation in the first two, and we do so later. Propan-1-ol gave, mainly, a species assigned structure (22) since it had the same spectrum as the radical anion obtained by one-electron reduction of 2-hydroxy-1-nitrobutane by the radical $\cdot\text{CMe}_2\cdot\text{OH}$. Of the three proton splittings, the smallest is assigned to the γ -proton, since the γ -proton splitting in the radical EtNO_2^- , (1), is of about this size whereas radicals lacking γ -protons [e.g. (3), (4), (6), (31)] also lack a splitting of this magnitude. (This argument is applied in subsequent assignments without being specified.) There was a trace of another radical from propan-1-ol which was probably the adduct formed by the species $\cdot\text{CHMe}\cdot\text{CH}_2\text{OH}$, but its resonances were not distinct enough for unambiguous attribution. The fact that ethanol and propan-1- and -2-ol each give (mainly) adducts formed from α -hydroxyalkyl radicals no doubt reflects the activating effect of the hydroxy-substituent on abstraction from adjacent C–H bonds by the hydroxyl radical.²²

Ethylene glycol gave two adducts. One had a spectrum identical to that observed during reduction of 2,3-dihydroxy-1-nitropropane by the radical $\cdot\text{CMe}_2\cdot\text{OH}$ and is therefore assigned the structure (23). The other is assigned the structure $\text{OCH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NO}_2^-$ (9), on the basis of small triplet (0.06 mT) and doublet (0.05 mT) splittings which are ascribed to the γ - and δ -protons, respectively; it is notable that the (aldehydic) δ -proton in the radical $\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHO}$ also gives an observable splitting.¹

When the concentration of nitromethane was 0.075M, these two adducts were present in relative concentrations ca. 1:1, but when the concentration of nitromethane was reduced to 0.01M only the adduct (9) was observed. These results are consistent with the evidence that the

¹⁵ D. J. Edge and R. O. C. Norman, *J. Chem. Soc. (B)*, 1970, 1083.

¹⁶ R. O. C. Norman and P. M. Storey, *J. Chem. Soc. (B)*, 1971, 1009.

¹⁷ D. Behar and R. W. Fessenden, *J. Phys. Chem.*, 1971, **75**, 2752.

¹⁸ R. O. C. Norman, P. M. Storey, and P. R. West, *J. Chem. Soc. (B)*, 1970, 1087.

¹⁹ M. McMillan and R. O. C. Norman, *J. Chem. Soc. (B)*, 1968, 590.

²⁰ K. Eiben and R. W. Fessenden, *J. Phys. Chem.*, 1968, **72**, 3387.

²¹ D. J. Edge, R. O. C. Norman, and P. M. Storey, *J. Chem. Soc. (B)*, 1970, 1096.

²² W. T. Dixon, R. O. C. Norman, and A. L. Buley, *J. Chem. Soc.*, 1964, 3625.

radical $\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{OH}$ undergoes dehydration to give the radical $\cdot\text{CH}_2\cdot\text{CHO}$ in a reaction which is acid-catalysed¹ but which is nevertheless fairly rapid even in neutral solution.²³ Thus, as the concentration of nitromethane is reduced, the radical $\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{OH}$ formed initially from the glycol is relatively more likely to undergo dehydration, and thereby yield radical (9) on trapping, than to be trapped directly by the *aci*-anion.

(b) *Ethers and acetals.* Diethyl ether, ethylene oxide, 1,4-dioxan, and trioxan each yielded one adduct. That from diethyl ether is assigned the structure (24), formed from the radical $\cdot\text{CHMe}\cdot\text{OEt}$, since the spectrum showed interaction with only one γ -proton; it was accompanied by a small concentration of the species $^{13}\text{HO}\cdot\text{CH}_2\text{NO}_2^-$. Ethylene oxide gave the radical (25), its spectrum being identical with that obtained by reducing 3-nitropropylene oxide with the radical $\cdot\text{CMe}_2\cdot\text{OH}$; the concentration of the adduct constituted about 80% of the observed mixture and small concentrations of the species MeNO_2^- and $\text{HO}\cdot\text{CH}_2\text{NO}_2^-$ were also present. The assignments of the spectra from 1,4-dioxan (Figure 1)

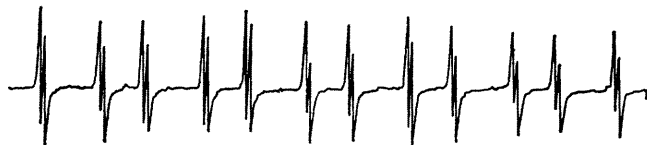


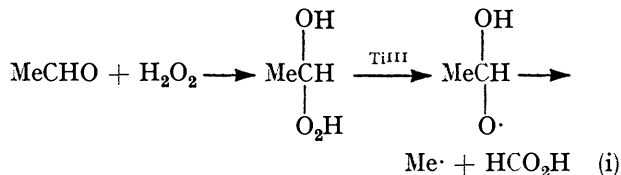
FIGURE 1 E.s.r. spectrum of the radical anion (26) at 20°

and trioxan to the radicals (26) and (8), respectively, are unambiguous; they were the only radicals detected.

(c) *Carbonyl compounds.* Acetaldehyde gave, in addition to the one-electron reduction product of nitromethane, three adducts. Their spectra were identical, within the limit of the experimental error, with those reported for the radicals (21) (see above) and (1)¹⁹ and (19),²⁴ which have previously been generated by, respectively, the one-electron reduction of nitroethane and the ultraviolet irradiation of an aqueous, alkaline solution of acetone and nitrite ion, so that the results indicate the mediation of the radicals $\text{CH}_3\text{CO}\cdot$, $\cdot\text{CH}_3$, and $\cdot\text{CHMe}\cdot\text{OH}$ in the oxidation of acetaldehyde.

The mediation of the acetyl radical during oxidation by the titanium(III) ion-hydrogen peroxide system has previously been inferred, although its spectrum was not observed.²⁵ However, the spectrum of the radical $\cdot\text{CHMe}\cdot\text{OH}$ has been observed,²⁶ as has that of the methyl radical when the aldehyde was pretreated with the peroxide;²⁵ it was suggested that the methyl radical arises from an intermediate α -hydroxyhydroperoxide as in reaction (i).²⁵ Since under our conditions the aldehyde and peroxide were introduced separately into the reaction cell, it seemed possible that the methyl

radical was generated in a different way, namely, by homolysis of the acetyl radical. However, contrary to expectation if this were the case, the observed ratio of the concentrations of the adducts formed by these two radicals showed no significant variation when the concentration of the trap was reduced fifteen-fold (*cf.* the benzoyloxy-phenyl radical conversion described later). Moreover, when hydrogen peroxide was replaced by sodium persulphate, the adduct from the acetyl radical was observed but that from the methyl radical was not. We infer that the reaction of acetaldehyde with hydrogen peroxide is fast enough to be responsible for the methyl radicals detected under our conditions (compare the rapid reaction of the aldehyde with hydroxylamine¹³). However, reduction in the concentration of nitromethane from 0.075 to 0.005M resulted in a decrease in the observed concentration of the adduct from the radical $\text{MeCO}\cdot$ relative to that from the radical $\cdot\text{CHMe}\cdot\text{OH}$, in accord with the view that the former, probably in the form of its hydrate $\cdot\text{CMe}(\text{OH})_2$, can yield the latter by donating one electron to another molecule of the aldehyde.



Acetone gave only one radical, the assignment of which as the species (10) is consistent with the observed interaction with two equivalent β - and two equivalent γ -protons.

(d) *Carboxylate ions.* Formate ion gave an adduct with only nitrogen and β -proton splittings which is assigned structure (11).¹⁵ Acetate ion gave mainly (>95%) an adduct identified²⁴ as (12); small concentrations of the nitromethane radical anion and of the adduct of the *aci*-anion with the hydroxyl radical were also detected, but there was no trace of the adduct with the methyl radical [compare the oxidation of acetate ion with the titanium(III) ion-persulphate system described later]. The spectrum from propionate ion showed the presence of two adducts, that with splitting from one γ -proton being assigned structure (29) and the other (splitting from two γ -protons) structure (13) [see also the reaction of succinate ion with the titanium(III) ion-persulphate system, described below]; the relative concentrations of the two were *ca.* 3 : 1. Pivalate gave only one adduct, assigned structure (14). Succinate ion gave mainly (>90%) an adduct attributed structure (32) on the basis of splitting from one γ -proton (Figure 2); a small concentration of the adduct with the hydroxyl radical was also observed. The predominant radicals detected from acrylate and methacrylate ions (>95%) are assigned structures (30) and (31), respectively, on the

²³ C. E. Burchill and K. M. Perron, *Canad. J. Chem.*, 1971, **49**, 2382.

²⁴ H. Zeldes and R. Livingston, *J. Amer. Chem. Soc.*, 1968, **90**, 4540.

²⁵ J. R. Steven and J. C. Ward, *Austral. J. Chem.*, 1967, **20**, 2005.

²⁶ A. L. Buley and R. O. C. Norman, *Proc. Chem. Soc.*, 1964, 225.

basis of the occurrence of splitting from one γ -proton in the former case and none in the latter; thus, we infer initial addition of the hydroxyl radical to the methylene group of each acid anion, to give the species $\text{HO}\cdot\text{CH}_2\cdot\text{CR}(\text{CO}_2^-)\cdot$ ($\text{R} = \text{H}$ or Me).



FIGURE 2 E.s.r. spectrum of the radical anion $-\text{O}_2\text{C}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2^-)\cdot\text{CH}_2\cdot\text{NO}_2^-$ at 20°

(e) *Esters*. The spectrum from ethyl formate showed the presence, in addition to MeNO_2^- and $\text{HOCH}_2\cdot\text{NO}_2^-$, of four radicals, namely, the adducts formed by the species $\cdot\text{CHMe}\cdot\text{OCHO}$, (27) (assigned on the basis of splitting from one γ -proton), $\cdot\text{CO}_2\text{Et}$, (15) (confirmed by the reduction of ethyl nitroacetate with the radical $\cdot\text{CMe}_2\cdot\text{OH}$), $\cdot\text{CO}_2^-$, (11) (as from formate ion), and $\cdot\text{CH}_2\text{Me}$, (2) (confirmed by the reduction of 1-nitropropane with the radical $\cdot\text{CMe}_2\cdot\text{OH}$). The relative concentrations of these four species were *ca.* 3 : 2 : 1 : 2. The radicals $\cdot\text{CHMe}\cdot\text{OCHO}$ and $\cdot\text{CO}_2\text{Et}$ have been detected from ethyl formate in the absence of the trap;²⁷ our result indicates that the latter undergoes decarboxylation readily (although not, apparently, decarbonylation, for there was no sign of the adduct from $\text{EtO}\cdot$; *cf.* ref. 28), and $\cdot\text{CO}_2^-$ presumably arises from rapid hydrolysis of ethyl formate.

t-Butyl formate gave mainly (>70%) a signal identical with one from pivalate ion and the sulphate radical anion (see later). The most likely common species from these two reactions is the t-butyl radical, for we should expect t-butyl formate and the hydroxyl radical to form $\cdot\text{CO}_2\text{Bu}^\dagger$ and thence²⁹ $\cdot\text{CMe}_3$ (*cf.* $\cdot\text{CH}_2\text{Me}$ from ethyl formate) and we should expect pivalate ion, like other carboxylates, to undergo oxidative decarboxylation with $\text{SO}_4^{\cdot-}$; we therefore attribute the spectrum to the adduct (3).

Ethyl acetate gave mainly (*ca.* 70%) the adduct (28) (one γ -proton splitting); the adduct with the hydroxyl radical was also present.

(f) *Halogen-containing compounds*. 2-Chloroethanol gave mainly (>90%) the adduct (9) formed by the radical $\cdot\text{CH}_2\cdot\text{CHO}$; the nitromethane radical anion was also present. Even when the concentration of nitromethane was raised to 0.075M, there was no trace of a spectrum which could be ascribed to the adduct formed by the radical $\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$, and when this result is compared with that from ethylene glycol, the conclusion

is reinforced that¹ the species $\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$ undergoes elimination of hydrogen chloride more readily than $\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{OH}$ undergoes dehydration.

2-Iodoethanol gave only one radical the spectrum of which was identical with that of the species²¹ $\text{O}_2\text{N}\cdot\text{CH}_2\text{CH}_2\cdot\text{NO}_2^-$ [and different from that of the radical (7) which we generated by reduction of 3-hydroxy-1-nitropropane by the radical $\cdot\text{CMe}_2\cdot\text{OH}$]. Thus, there is no evidence for formation of the radical $\cdot\text{CH}_2\text{CH}_2\text{OH}$ by the one-electron reduction of the iodo-compound or for formation of $\cdot\text{CH}_2\text{CHO}$ by elimination of hydrogen iodide from $\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{I}$ (*cf.* the behaviour of 2-chloroethanol). However, the result is in accord with the view that the species $\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{I}$, formed initially, undergoes homolysis to release an iodine atom¹ which is a sufficiently good oxidant to convert the *aci*-anion into the radical $\cdot\text{CH}_2\text{NO}_2$; this is then trapped by more of the *aci*-anion (*cf.* the reaction²¹ of the *aci*-anion with $\text{SO}_4^{\cdot-}$).

Chloral hydrate gave mainly (*ca.* 85%) a spectrum identical with that from trichloroacetate ion with the sulphate radical anion (see below) and assigned to the adduct (18) from the radical $\cdot\text{CCl}_2\cdot\text{CO}_2^-$; evidently the initially formed radical, presumed to be $\cdot\text{C}(\text{OH})_2\cdot\text{CCl}_3$, undergoes loss of hydrogen chloride²² so rapidly that it is not trapped in significant amount. The adduct with the hydroxyl radical was also present.

Carbon tetrachloride gave mainly (*ca.* 60%) a spectrum assigned to the adduct (17) with the trichloromethyl radical; this adduct was also present when chloroform was oxidised but constituted only about 10% of the mixture, the predominant radical being that formed by addition of the hydroxyl radical. Chloroacetate ion gave mainly (*ca.* 85%) a spectrum attributed to the adduct (34) on the basis of its splitting from one γ -proton; the adduct with the hydroxyl radical was also present.

Titanium(III) Ion-Persulphate System.—The spectra observed during oxidation of each of the compounds treated with the titanium(III) ion-persulphate system showed the presence, in addition to adducts derived from those compounds and the nitromethane *aci*-anion, of the nitromethane radical anion and the dimeric species $\text{O}_2\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NO}_2^-$; the latter presumably arises by the abstraction of an electron from the *aci*-anion by $\text{SO}_4^{\cdot-}$ followed by trapping of the resultant nitromethyl radical by more of the *aci*-anion.²¹

Acetate ion gave mainly (>95%) the radical (1); there was no trace of a spectrum from trapping of the radical $\cdot\text{CH}_2\cdot\text{CO}_2^-$. Propionate ion gave mainly (*ca.* 90%) the adduct (2) from the ethyl radical; there was no trace either of adducts from the carboxylate-containing radicals $\cdot\text{CHMe}\cdot\text{CO}_2^-$ and $\cdot\text{CH}_2\text{CH}_2\text{CO}_2^-$ or of one from the radical $\text{EtCO}_2\cdot$ (compare $\cdot\text{CO}_2\text{Et}$ from ethyl formate, which is trapped as well as yielding the ethyl radical). α -Chloropropionate ion gave mainly (70%) a spectrum identical with that from reduction of 2-chloro-1-nitropropane by the radical $\cdot\text{CMe}_2\cdot\text{OH}$ and therefore

²⁷ A. R. Metcalfe and W. A. Waters, *J. Chem. Soc. (B)*, 1967, 340.

²⁸ P. Gray and J. C. J. Thynne, *Nature*, 1961, **191**, 1357.

²⁹ D. Griller and B. P. Roberts, *Chem. Comm.*, 1971, 1035.

TABLE 1
Hyperfine splitting constants and line-widths (mT) for radicals ^a of the type RCH₂NO₂⁻

Radical	R	<i>a_N</i> (1)	<i>a_H</i> (CH ₂)	<i>a_H</i> (other)	ΔH
1	Me	2.60	0.97	0.05 (3H)	0.02
2	Et	2.54	1.01	{0.06 (2H) 0.03 (3H)}	0.01
3 ^b	Me ₃ C	2.37	0.87		0.03
4	Ph	2.59	0.95		0.025
5	CH ₂ -OH	2.55	1.07	0.04 (2H)	{0.01 0.02}
6	CMe ₂ -OH	2.43	1.01		{0.02 0.07}
7	CH ₂ CH ₂ -OH	2.57	1.00	{0.055 (2H) 0.027 (2H)}	0.015
8	C ₃ H ₅ O ₃ ^e	2.51	0.96	0.06 (1H)	0.02
9	CH ₂ -CHO	2.60	1.05	{0.06 (2H) 0.05 (1H)}	0.02
10	CH ₂ COMe	2.60	1.07	0.06 (2H)	0.015
11	CO ₂ ⁻	2.47	0.86		0.015
12	CH ₂ CO ₂ ⁻	2.60	1.00	0.07 (2H)	0.015
13	CH ₂ CH ₂ CO ₂ ⁻	2.55	1.02	0.06 (2H)	0.025
14	CH ₂ CMe ₂ CO ₂ ⁻	2.60	0.95	0.08 (2H)	0.02
15	CO ₂ Et	2.50	0.78		0.02
16 ^d	CH ₂ Cl	2.53	1.04	0.06 (2H)	{0.01 0.025}
17 ^d	CCl ₃	2.21	0.77		0.02
18	CCl ₂ CO ₂ ⁻	2.37	0.92		{0.02 0.07}
19	COMe	2.43	0.77		0.02
20	PhCO ₂	2.40	0.74		0.025

^a *g* 2.0050 except where stated. ^b *g* 2.0049. ^c Trioxanyl. ^d *g* 2.0052.

TABLE 2
Hyperfine splitting constants and line-widths (mT) for radicals ^a of the type CXYZ-CH₂NO₂⁻

Radical	X	Y	Z	<i>a_N</i> (1)	<i>a_{β-H}</i> (1)	<i>a_{β-H}</i> (1)	<i>a_{γ-H}</i> (1)	ΔH
21	H	Me	OH	2.51	1.12	0.97	0.06	{0.025 0.04}
22	H	Et	OH	2.52	1.16	0.92	0.06	{0.025 0.04}
23	H	CH ₂ OH	OH	2.52	1.17	0.87	0.06	{0.02 0.03}
24	H	Me	OEt	2.50	1.21	0.86	0.06	{0.025 0.04}
25	H	CH ₂ O ^b		2.58	1.08	0.89		{0.025 0.025}
26	H	CH ₂ OCH ₂ CH ₂ O ^c		2.54	1.26	0.73	0.06	{0.02 0.02}
27	H	Me	OCHO	2.47	1.29	0.62	0.07	{0.025 0.03}
28	H	Me	OAc	2.47	1.27	0.68	0.06	{0.03 0.04}
29	H	Me	CO ₂ ⁻	2.51	1.44	0.68	0.06	{0.02 0.03}
30	H	CH ₂ OH	CO ₂ ⁻	2.53	1.32	0.76	0.07	{0.02 0.03}
31	Me	CH ₂ OH	CO ₂ ⁻	2.41	1.10	0.79		{0.035 0.045}
32 ^d	H	CH ₂ CO ₂ ⁻	CO ₂ ⁻	2.51	1.22	0.94	0.06	{0.02 0.055 ^e }
33 ^f	H	Me	Cl	2.47	1.34	0.66	0.06	{0.025 0.04}
34	H	CO ₂ ⁻	Cl	2.49	1.64	0.41	0.08	{0.015 0.035}

^a *g* 2.0050 except where stated. ^b Oxiranyl. ^c 1,4-Dioxanyl. ^d *g* 2.0052. ^e At 20°; see text for temperature dependence. ^f *g* 2.0051.

attributed to the adduct (33) formed by the radical $\cdot\text{CHMe}\cdot\text{Cl}$. The spectrum from pivalate ion showed the presence of the radical (14) (*ca.* 15%) and a species (*ca.* 30%) with identical splitting constants to one from *t*-butyl formate and the hydroxyl radical and therefore assigned structure (3). Succinate ion gave mainly (90%) the same spectrum as one radical from propionate

ion with the hydroxyl radical and therefore assigned to the species (13) (see earlier).

The spectrum from chloroacetate ion showed the presence of about 40% of the adduct (16) from the radical $\cdot\text{CH}_2\text{Cl}$, its spectrum being characterised by its identity with that from 2-chloronitroethane and the radical $\cdot\text{CMe}_2\cdot\text{OH}$. [The broadening of the central line

of the 1:2:1 triplet with respect to the outside lines (Table 1) was more clearly seen when the radical was generated by the latter method because of overlap with lines from other radicals under the former conditions.] Trichloroacetate ion gave a spectrum (*ca.* 40%) identical to that from chloral hydrate and the hydroxyl radical and attributable (see earlier) to the adduct (18), but there was no trace of the adduct (17) from the trichloromethyl radical in the complex mixture.

Benzoate ion gave mainly a mixture of two adducts, which constituted about 90% of the observed mixture. One was identified as that from the phenyl radical, (4), since the same spectrum was obtained by the reduction of phenylnitromethane with the radical $\cdot\text{CMe}_2\text{OH}$. The second radical we believe to be the adduct, (20), with the benzoyloxyl radical, on the grounds that the ratio of the concentrations of this adduct and the adduct (4) increased as the concentration of nitromethane was increased, as follows: 2:1 (0.01M), 3:1 (0.015M), 6:1 (0.03M), consistent with the view that the benzoyloxyl radical can be trapped to give the observed adduct or can undergo decarboxylation to give the phenyl radical. It is also notable that the spectrum ascribed to the adduct with the benzoyloxyl radical has lower values for both a_N and $a(\text{CH}_2)$ than that for the adduct with the phenyl radical, just as in the case of the corresponding adducts from these radicals with *N*-*t*-butyl methylene nitrene.³⁰ Finally, we considered the possibility that the adduct (20) is formed, not from the benzoyloxyl radical and the *aci*-anion, but from the benzoate anion and the nitromethyl radical, since both the last species are present under the reaction conditions and nitroalkyl radicals are known to react with nucleophiles³¹ (*e.g.* ammonia). However, we rejected it since the corresponding adducts are not formed from acetate ion, propionate ion, *etc.*, although they are likely to be better nucleophiles than benzoate ion (since they are derived from slightly weaker acids).

Comparison of the results of reactions of carboxylate ions with the hydroxyl radical with those for reactions with the sulphate radical anion reinforces the conclusion reached previously that the latter species has a relatively greater capacity for abstracting an electron.¹⁸ Thus, with the hydroxyl radical, acetate and propionate ions gave adducts only from radicals derived by abstraction of hydrogen from C-H, whereas, with the sulphate radical anion, they gave adducts only from radicals formed by oxidative decarboxylation. Of the carboxylate ions studied, only trichloroacetate resisted oxidative decarboxylation, at least at a rate great enough to give a detectable concentration of the adduct from the trichloromethyl radical.

Magnetic Inequivalence owing to Chirality.—All the radicals listed in Table 2 have two, unequal β -proton splittings, and in most cases the inner lines of the four

resonances to which these protons give rise are broadened with respect to the outermost lines. There could be two reasons for the inequality. First, the radicals might preferentially adopt conformations in which the β -C-H bonds make different dihedral angles with the $2p_z$ orbital on nitrogen, hence giving different splittings providing that the interchange of positions of the two β -protons occurs at a rate below the slow-exchange limit or (for the cases where the line-widths are unequal) just above that limit. Secondly, the inequality could result from the chirality of the neighbouring carbon atom; that is, the two β -protons could have different (average) magnetic environments even when conformational interconversion is rapid (above the fast-exchange limit). This phenomenon has been observed before for nitronyl-nitroxides³² and some simple nitroxides.³³

Now, of the radicals we have examined, every one with chiral carbon adjacent to the β -methylene group has non-equivalent β -protons (Table 2) whereas no radical without chiral carbon does so, although in four cases there is an alternating line-width effect (Table 1). This is certainly convincing circumstantial evidence that the unequal splittings are associated with chirality; it would be surprising, for example, if radicals as structurally similar as (8), from the trioxanyl radical, and (26), from the 1,4-dioxanyl radical, differed in having equivalent and inequivalent β -protons, respectively, for steric reasons, whereas it is reasonable that the difference should be associated with the absence and presence, respectively, of chiral carbon.

To seek further information, we studied the effect of temperature on the line-widths in the spectrum of the radical (32) [$-\text{O}_2\text{C}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2^-)\cdot\text{CH}_2\text{NO}_2\cdot^-$]. If the non-equivalence arises from conformational barriers only, then an increase in temperature should cause more rapid interchange between conformations and thus a tendency for coalescence of the inner two lines of the two doublets from the β -protons to give, ultimately, a 1:2:1 triplet. However, we found that raising the temperature resulted in a sharpening of each of the inner two lines; their widths were 0.07 (10°), 0.055 (20°), and 0.035 mT (40°), while the widths of the outer resonances remained constant (0.02 mT). These results, while inconsistent with an explanation based only on restricted rotation, are in accord with one based on the presence of chiral carbon, as the following argument shows.

Suppose that there is a conformation of minimum energy, *A*, in which the β -C-H bonds subtend dihedral angles of θ and ϕ ($\phi + \theta \sim 120^\circ$) with the nitrogen $2p_z$ orbital and the protons have splitting constants a_1 and a_2 , respectively. There is another conformation, *B*, in which the dihedral angles are reversed for H^1 and H^2 . Now, if X is not chiral, conformation *B* is also one of minimum energy and is associated with splitting constants a_2 and a_1 for H^1 and H^2 , respectively. However,

³⁰ G. R. Chalfont, M. J. Perkins, and A. Horsfield, *J. Chem. Soc. (B)*, 1970, 401.

³¹ N. H. Anderson, M. McMillan, and R. O. C. Norman, *J. Chem. Soc. (B)*, 1970, 1075.

³² R. W. Kreilick, J. Becher, and E. F. Ullman, *J. Amer. Chem. Soc.*, 1969, **91**, 5121.

³³ P. Tordo, M. P. Bertrand, and J.-M. Surzur, *Tetrahedron Letters*, 1970, 1799.

if X is chiral, two additional factors must be considered. First, the magnetic environments of H¹ in A and H² in B are not the same, and likewise those of H² in A and H¹ in B differ; thus, the splitting constants for conformation B might be a_1' ($\neq a_2$) and a_2' ($\neq a_1$). Secondly, conformations A and B may differ in energy as a result of differences in compressional forces; thus, C rather than B might represent a minimum in the energy profile, again leading to a different pair of splitting constants from those for A. Then the situation which can arise is shown in Figure 3; (a)—(d) represent the resonances

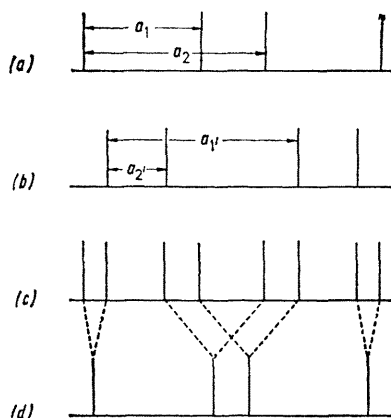
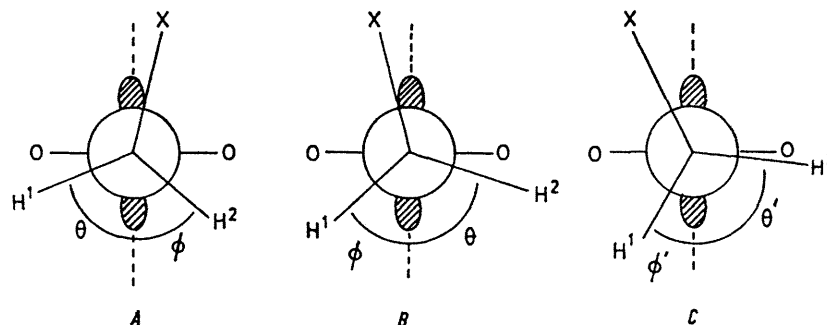


FIGURE 3 Possible splitting patterns for the species A and B (or C) (X is chiral)

from the β -protons in (a) conformation A, (b) conformation B or C, (c) the slow-exchange limit for both



conformations (equally weighted), and (d) the fast-exchange limit. Thus, as the temperature rises, the spectrum should change from eight sharp lines, as in (c), to a situation in which the lines are coalescing in pairs (as shown by the dotted lines) to a four-line spectrum of equally sharp lines, (d). In our case, between 10 and 40°, the rates are such that coalescence has occurred and the appropriate resonances are gradually sharpening towards the situation in (d). The crucial point is that the pairs of lines which coalesce at the centre of the spectrum are far more widely separated than the corresponding pairs in the wings, so that the two central resonances are broadened with respect to the outer ones; indeed, the constancy of the width of the outer resonances shows that, at least to a close approximation,

$a_1 + a_2 = a_1' + a_2'$. (The argument in this paragraph can be extended to the situation in which, instead of their being only two conformations, there is a range of conformations of different energies which lead to two average conformations when suitably weighted.)

We have no reason to doubt that the other radicals in Table 2 owe their unequal β -proton splittings to the chiral carbon atom and the inequalities in the line-widths in their spectra to restricted rotation; restricted rotation is also implicated in radicals (5), (6), (16), and (18) in Table 1. Unequal β -proton splittings have been noted for several other radicals which contain chiral carbon and have been attributed to restricted rotation, and although the alternative explanation based on the effect of chiral carbon cannot be accepted in such cases without further investigations such as we have carried out for radical (32), nevertheless attention should be paid to the possibility. For example, it would seem very likely that the non-equivalence of the β -protons in the radicals $O_2N\cdot CHMe\cdot CH_2NO_2^{\cdot-}$, $O_2N\cdot CHEt\cdot CH_2NO_2^{\cdot-}$, and $HO\cdot CHMe\cdot CH_2NO_2^{\cdot-}$ is associated with the presence of chiral carbon, whereas the varying line-widths in the spectra of the species $O_2N\cdot CH_2\cdot CMe_2NO_2^{\cdot-}$ and $HO\cdot CH_2\cdot CMe_2NO_2^{\cdot-}$ reflect restricted rotation;²¹ and the non-equivalence of the β -methylene protons in the polymeric radical $\cdot CMe(CO_2Me)\cdot CH_2\cdot [CMe(CO_2Me)\cdot CH_2]_n\cdot OH$ may be induced by the adjacent chiral carbon rather than be the result³⁴ of restricted rotation.

The Utility of the Nitromethane aci-Anion as a Radical Trap.—The *aci*-anion from nitromethane suffers from one obvious disadvantage as a trap for radicals, namely,

that it can only be used in basic solution. Within this context, however, it has several attractive features as a trap.

First, it is readily available by dissolution of nitromethane in base. Secondly, the spectra, at least under the conditions we have used, are intense, with narrow lines; moreover, these spectra were obtained at a pH (≤ 9.5) below the pK_a of nitromethane (10.2³⁵), so that the concentration of the trap could be increased several-fold if necessary. Although, in general, nitro radical-anions are not so long-lived as the nitroxides obtained with nitroso-compounds or nitrones as traps, it is

³⁴ H. Fischer, *Polymer Letters*, 1964, **2**, 529.

³⁵ R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439.

notable that they are stable enough to be observed by e.s.r. in a static system when generated, for example, electrochemically.³⁶

Thirdly, radicals involving a variety of elements—carbon, oxygen, nitrogen, sulphur—can be successfully trapped; we have also found that phosphorus radicals (PO_3^{2-} , HPO_2^{-} , PhPO_2^{-}) are trapped, and shall discuss these results elsewhere. Further, there is evidence that the presence of radicals which are effective one-electron oxidants but are not trapped to give adducts can nevertheless be recognised by formation of the species $\text{O}_2\text{N}\cdot\text{CH}_2\text{CH}_2\cdot\text{NO}_2^{-}$, as with SO_4^{-} and, as we have argued, the iodine atom.

Fourthly, the splitting constants for the nitrogen nucleus and the β -protons vary significantly with the nature of the radical which has been incorporated. This makes it possible to observe individual spectra in a mixture of radicals (small variations in g -factor are also of assistance in this respect); indeed, we were in several cases able to detect four radicals and, in one case (from ethyl formate), six.

Moreover, there are clear indications that these two splittings vary systematically with structure. For example, addition of radicals of the type $\text{RCH}_2\cdot$ gives species with a_N in the range 2.53—2.60 mT and $a_H(\text{CH}_2)$ in the range 0.97—1.10 mT; for addition of the carbonyl-containing radicals $\cdot\text{CO}_2^{-}$, $\cdot\text{CO}_2\text{Et}$, and $\cdot\text{COMe}$, the corresponding ranges are 2.42—2.50 and 0.77—0.86 mT; aminyl radicals, $\text{RNH}\cdot$, give species with comparable values of a_N (2.47—2.50 mT) but significantly higher values of $a_H(\text{CH}_2)$ (0.91—0.95 mT);¹⁴ and the addition of sulphur-centred radicals gives species with especially low parameters [a_N 2.20, 2.40; $a_H(\text{CH}_2)$ 0.745, 0.60 mT for $\text{SO}_3^{\cdot-}$ and $\text{S}_2\text{O}_3^{\cdot-}$, respectively¹⁶]. Further, a_N shows systematic trends even within a closely related group of radicals; for example, for addition of $\text{Me}\cdot$, $\text{Et}\cdot$, and $\text{Me}_3\text{C}\cdot$ the values are 2.60, 2.54, and 2.37 mT, and, for $\cdot\text{CH}_2\cdot\text{OH}$, $\cdot\text{CHMe}\cdot\text{OH}$, and $\text{CMe}_2\cdot\text{OH}$, 2.55, 2.51, and 2.43 mT. (A possible explanation for the decrease in a_N with increase in size of the radical, $\text{R}\cdot$, which adds, is that a large group R tends to reduce the deviation from coplanarity about the nitrogen atom³⁷ in order to relieve compressional forces.) These structural correlations imply that it should often be possible to gain information about the nature of the radical which has been trapped from a_N and $a_{\beta-H}$. For the addition of carbon radicals, two further, complementary pieces of information about the structure of the trapped species may be available from the hyperfine splittings. One is

the recognition, from unequal β -proton splittings, that a chiral carbon is adjacent to the methylene group in $\text{RCH}_2\text{NO}_2^{\cdot-}$. The other is that, if the trivalent carbon atom is attached to one or more protons, appropriate γ -proton splittings (*ca.* 0.05 mT) are to be expected (only in one case, addition of the oxiranyl radical, was the expected γ -proton splitting not observed); moreover, in some cases even longer-range splittings may be detected, as for addition of the radicals $\cdot\text{CH}_2\text{Me}$, $\cdot\text{CH}_2\text{CH}_2\text{OH}$, and $\cdot\text{CH}_2\text{CHO}$.

Finally, it should usually be possible to obtain confirmatory evidence for the structure assigned to the trapped radical, $\text{R}\cdot$, by independent generation of the species $\text{RCH}_2\text{NO}_2^{\cdot-}$, for example, by reducing the nitro-compound RCH_2NO_2 with the radical $\cdot\text{CMe}_2\cdot\text{OH}$.

EXPERIMENTAL

A Varian E-3 spectrometer with 100 kHz modulation was employed for the e.s.r. measurements. Hyperfine splittings were measured to within ± 0.01 mT both directly and by comparison with an aqueous solution of Fremy's salt (a_N 1.3091 ± 0.0004 mT³⁸) which was also used for the determination of g -factors to within ± 0.0001 (g ³⁹ 2.0055). Spectrum simulation with a programme kindly supplied by Dr. M. F. Chiu was used to confirm the splitting constants and line-widths and to determine relative concentrations of radicals in some cases.

A three-entry single-stage mixing chamber was used. One stream contained 0.02M-titanium(III) chloride and disodium ethylenediaminetetra-acetate (6 g/l), the pH being adjusted to *ca.* 9 with ammonia (d 0.880), or, in the experiments with esters and halogen-containing compounds, sodium carbonate. This stream also contained the appropriate organic compound. The second stream contained 0.033M-hydrogen peroxide or 0.025M-sodium persulphate and the third stream contained nitromethane (0.01M except where stated in the text) adjusted to pH 9 with ammonia or sodium carbonate (see above).

Except for those listed below, all materials were reagent grade and were used without purification. Iodohydrin was prepared as previously reported,⁴⁰ 2,3-dihydroxy-1-nitropropane and 3-nitropropylene oxide were prepared by the methods of Sokovishina *et al.*,⁴¹ and 2-hydroxy-1-nitrobutane, 2-chloro-1-nitropropane, 2-chloronitroethane, phenylnitromethane, and 3-hydroxy-1-nitropropane were prepared by standard procedures. Ethyl nitroacetate was prepared by the method of Arndt and Rose⁴² and *t*-butyl formate by that of Stevens and van Es.⁴³

The tenure of an I.C.I. Fellowship (by J. P. L.) is gratefully acknowledged.

[2/248 Received, 7th February, 1972]

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³⁹ J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, 1966, **45**, 654.

⁴⁰ A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc. (B)*, 1969, 400.

⁴¹ I. J. Sokovishina, V. V. Perekalin, O. M. Lerner, and L. M. Andreeva, *Zhur. Org. Khim.*, 1965, **1**, 636 (*Chem. Abs.*, 1965, **63**, 5573).

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⁴³ W. Stevens and A. van Es, *Rec. Trav. chim.*, 1964, **83**, 1287.