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Electron Spin Resonance Studies. Part XX.¹ The Generation of Organic Radicals by the One-electron Reduction of Aliphatic Halogeno-compounds in Aqueous Solution

By A. L. J. Beckwith and R. O. C. Norman,* Department of Chemistry, The University of York, Heslington, York YO1 5DD

The carbon dioxide radical-anion, which can be obtained in aqueous solution through the oxidation of sodium formate by the hydroxyl radical produced from titanium(III) ion and hydrogen peroxide, is an effective one-electron reducing agent for many aliphatic halogeno-compounds; we have observed the e.s.r. spectra of a number of organic radicals formed in this way. The method seems to be generally applicable to iodo-compounds, but with bromoor chloro-compounds there is a requirement for a substituent which is capable of stabilising the resulting radical. The conjugate acid of the carbon dioxide radical-anion is a somewhat less effective reducing agent, and the radical ·CMe₂OH is even less effective.

THE REDUCTIVE elimination of halide ion from an organic halogeno-compound to give the corresponding organic radical can be achieved with hydrated electrons,² sodium naphthalenide,³ and lithium alkyls,⁴ or by γ -irradiation⁵ or photolysis.⁶ However, none of these methods appears readily applicable to the study of the e.s.r. spectra of these radicals; for this purpose, it is desirable to use water as the solvent since it is effectively inert towards organic radicals, and to use a flow-cell technique in which the radicals can be generated continuously so as to overcome the problem associated with their rapid rates of decay. We now report that a convenient method for these conditions is the use of the carbon dioxide radical-anion, $\cdot CO_2^-$, or its conjugate acid, $\cdot CO_2H$, according to the pH which is required.

The latter radical is generated by mixing an acidic solution of titanium(III) ions and formic acid with one of hydrogen peroxide; the one-electron reduction of the peroxide by titanium(III) gives the hydroxyl radical which oxidises formic acid to •CO₂H.¹ This radical can be observed by e.s.r. spectroscopy¹ as a doublet, g = 2.0002. When weakly basic conditions are employed, the e.s.r. spectrum consists of a singlet, and this, together with the facts that the g-factor (2.0003) is closely similar to that of $\cdot CO_2H$ and significantly below the free-spin value 1 and that $\cdot CO_{2}H$ is a relatively strong acid,⁷ indicates that this is the spectrum of the carbon dioxide radical-anion.[†] When a suitable halogeno-compound is included, the spectrum of •CO₂H or $\cdot CO_2^{-}$ is partially or completely quenched and that of the radical derived by the one-electron reduction of the halogeno-compound with elimination of halide ion is observed.

[†] The isotropic g-factor obtained from the e.s.r. spectrum of the \cdot CO₂⁻ radical trapped in sodium formate at room temper-ature is ⁸ 2.0006. In this case there is also interaction with the sodium nucleus in an adjacent cation, and this may underlie the slightly higher g-factor than is obtained under our conditions.

¹ Part XIX, R. O. C. Norman and P. R. West, preceding

paper.
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 Phys. Chem., 1965, 69, 289.
 ^a G. D. Sargent, J. N. Cron, and S. Bank, J. Amer. Chem. Soc.,
 1966, 88, 5363; J. F. Garst, P. W. Ayers, and R. C. Lamb, *ibid.*,
 1966, 88, 4260.

Suitable experimental conditions are obtained by use of a simple mixing chamber and flow-cell⁹ in which, for reductions by $\cdot CO_2^-$, are mixed aqueous solutions containing (i) 0.008M-titanium(III) chloride, 0.016M-disodium ethylenediaminetetra-acetate, and 0.5M-sodium formate, with the appropriate amount of potassium carbonate to give a pH value in the range 7-8, and (ii) 0.008M-hydrogen peroxide and a 0.01-0.04M-solution of the halogeno-compound. Ammonia can be used in place of potassium carbonate as the buffer, but the e.s.r. spectra are then generally less intense and, with some halogeno-compounds, there is the possibility that ammonolysis may occur. For reductions by ·CO₂H, disodium ethylenediaminetetra-acetate and the buffering agent are omitted and the titanium(III)-containing reactant is treated with sulphuric acid to give a pH value in the range 1-2. Where we made comparisons, reduction in the acidic medium either gave less intense spectra than in the weakly basic medium or, with 3-iodopropionic acid, occurred too slowly to give a detectable spectrum of the radical •CH₂CH₂CO₂H, although the conjugate base of this radical was observed in the basic medium. We attribute these differences to the fact that the carbon dioxide radical-anion is a more powerful reducing agent than its conjugate acid.

We were also able to observe the spectra of radicals from halogeno-compounds by containing these compounds in a third solution which was mixed with the titanium(III)- and peroxide-containing reactants either at the same time as these were mixed or very shortly afterwards. The e.s.r. absorption was weaker under the latter conditions than under the former, and the former method would be appropriate for the reduction of those halogenocompounds which react fairly rapidly with either titanous ion or hydrogen peroxide.

⁶ D. W. Skelly, R. G. Hayes, and W. H. Hamill, J. Chem. Phys., 1965, **43**, 2795; T. R. Suttle and R. J. Lontz, *ibid.*, 1967, **46**, 1539; M. Kashiwagi, Bull. Chem. Soc. Japan, 1966, **39**, 2051; R. F. C. Claridge and J. E. Willard, J. Amer. Chem. Soc., 1966, **50**, 2464, 1926, **50**, 510

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⁸ D. W. Ovenall and D. H. Whiffen, Mol. Phys., 1961, 4, 135. ⁹ W. T. Dixon and R. O. C. Norman, J. Chem. Soc., 1963, 3119.

⁴ A. R. Lepley, J. Amer. Chem. Soc., 1968, **90**, 2710; H. R. Ward and R. G. Lawler, *ibid.*, 1967, **89**, 5518; D. Bryce-Smith, J. Chem. Soc., 1956, 1603.

This method of reduction appears to be generally applicable to aliphatic iodo-compounds, but not to bromo- or chloro-compounds unless these contain substituents which can stabilise the resulting radical. Thus, with equal concentrations of the following halogenocompounds in the weakly basic medium, methyl iodide and ethyl iodide gave the corresponding alkyl radicals, the spectrum of the former being accompanied by that of residual carbon dioxide radical-anion; with ethyl bromide, the spectrum of the carbon dioxide radicalanion was essentially completely unquenched and that of the ethyl radical could not be detected; allyl bromide and bromoacetic acid gave spectra of the derived radicals with no trace of residual carbon dioxide radical-ion; and trichloroacetic acid gave the spectrum of the radical •CCl₂•CO₂H whereas mono- or di-chloroacetic acid were unaffected. The order of the ease of reductive cleavage indicated by these results, I > Br > Cl, is the same as that for reaction of aliphatic halogeno-compounds with the hydrated electron.² p-Iodobenzoic acid was not reduced under either the acidic or the basic conditions.

We also investigated the reducing properties of the radical ·CMe_oOH, generated by the oxidation of isopropyl alcohol by the titanium(III)-peroxide system,⁹ towards a sample selection of halogeno-compounds in acidic solution. With methyl iodide or 2-iodoethanol, the spectrum of •CMe₂OH was unquenched and that of the methyl or hydroxyethyl radical could not be detected. However, bromoacetic acid and trichloroacetic acid gave the radicals •CH₂CO₂H and •CCl₂•CO₂H, respectively. When a solution containing both bromoacetic acid and maleic acid was added subsequent to oxidation of isopropyl alcohol by the titanous-peroxide system, the spectrum observed was that of the radical (I) $[a_{\rm H}(1),$ 20.6 Oe; $a_{\rm H}(1)$, 10.8 Oe; g, 2.0033]. Thus, the radical •CMe₂OH adds to maleic acid in preference to reducing bromoacetic acid and, in general, it is a less powerful reducing agent for halogeno-compounds than both $\cdot CO_2^-$ and $\cdot CO_2H$.



The hyperfine splitting constants and g-factors for the radicals we have generated by the reductive method are given in the Table, together with the assigned structures. Where these radicals have previously been examined in solution by e.s.r. spectroscopy, the values for the parameters are in close agreement with those reported.¹⁰ The following are the more notable features of the data.

(a) The g-factors for those radicals in which the tervalent carbon atom is attached only to hydrogen and saturated carbon atoms are hardly greater than the free-spin value, while those in which the tervalent carbon

atom is conjugated to a carboxylic acid or carboxylateion group have g-factors in the range 2.0033-2.0034, reflecting delocalisation of the unpaired electron on to the carbonyl-oxygen atom. The constancy of the value for radicals of the latter class indicates that the g-factor can usefully be employed in the recognition of such radicals by e.s.r. spectroscopy.¹¹

Radicals formed by reductive elimination from halogenocompounds and their hyperfine splitting constants (Oe) and g-factors.

Halogeno-	Radical	a	<i>do</i>	a
Compound	CH	иα-н	иВ-н	5
Mel	·CH3	22.9		2.0025
EtI	·CH ₂ ·CH ₃	$22 \cdot 2$	27.1	2.0025
CH.=CHCH.Br	·CH,·CH:CH,	{13·7 •	4.1	2.0026
		(14.0		
CH ₂ BrCO ₂ H	·CH2·CO2H	21.6		2.0033
	·CH ₂ ·CO ₂ -	21.6		2.0033
CH ₃ CHBrCO ₂ H	•CHMe•CO ₂ H	20.2	24.8	2.0033
0 1	·CHMe·CO ₅ -	20.4	24.9	2.0033
ICH ₂ CH ₂ CO ₂ H	•CH2•CH2•ČO2~	$22 \cdot 2$	25.8	2.0026
CH,CH,CHBrCO,H	•CHEt•CO.H	20.1	24.8	2.0033
• • •	·CHEt·CO.~	20.2	23.8	2.0033
(CH ₃) ₂ CBrCO ₂ H	·CMe ₂ ·CO ₂ -		22.0	2.0034
HO,C-CH,-CHBr	•CH(CH,•CO,H)•CO,H	20.7	21.9	2.0033
CO.H	·CH(CH, CO, -), CO, -	20.3	23.2	2.0033
ICH CH OH	·CH.·CH.·OH	22.0	28.0	2.0026
ICH,CH,CH,OH	·CH.[CH.].OH	22.0	27.1	2.0026
CI.C.CO.H	·CCI, CO, H	b		2.0082
5 2	·CCl ·CO -	С		2.0079
Cl ₃ C·CH(OH) ₂	·CCl ₂ ·CH(OH) ₂	d	8.0	2.0076
^a See text. ^b a	$a_{\rm CI}(2)$, 3.0 Oe. $c_{\rm CI}(2)$	e), 2·9	Oe.	$a_{C1}(2)$

(b) The g-factors of the three radicals in which the tervalent carbon atom is bonded to chlorine are significantly larger than the remainder as a result of the relatively large spin-orbit coupling constant for chlorine. It was not possible to resolve the resonances due to interaction with 35 Cl from those due to 37 Cl, although the resonances in the wings of the spectrum were somewhat broader than those near the centre.

(c) Not only are the g-factors for the radicals \cdot CHMe \cdot CO₂H and its conjugate base the same but, further, the splittings due to the methyl-group protons do not differ significantly, which indicates ¹² that the carboxylic-acid and the carboxylate-ion groups have approximately the same capacity to delocalise the unpaired electron.

(d) The splitting due to the β -protons is larger in the radical \cdot CHEt \cdot CO₂H than in its conjugate base, showing that the steric requirements of -CO₂H and -CO₂⁻ differ somewhat.¹⁰

(e) Two of the methylene protons in the allyl radical interact to a different extent from the other two. This is reasonable, for the *exo*-pair, marked H(1) in structure (II), are differently situated from the *endo*-pair, marked H(2) in structure (II). The appropriate resonances are all sharp (see Figure), as is also the case ¹³ at -120° , showing that, even at room temperature, interconversion of the two planar configurations (II) and (III), which

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¹² H. Fischer, Z. Naturforsch., 1965, 20a, 428.

¹³ R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1963, **39**, 2147.

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can occur by rotation about one of the C-C bonds, is less rapid than the hyperfine splitting interval [2.8 (14.6-13.7) Mc./sec.] *i.e.*, $< ca. 10^{6}$ /sec.



(f) The differences in the spectra obtained from trichloroacetic acid in weakly basic and in acidic conditions, though small, are real and show that, at a pH value in the range 1—2, the radical is $\cdot \text{CCl}_2 \cdot \text{CO}_2\text{H}$ and



E.s.r. spectrum of the allyl radical in aqueous solution at room temperature

not the conjugate base. Thus, this radical, unlike trichloroacetic acid itself, is a sufficiently weak acid to exist essentially entirely as such in an aqueous medium of this pH.

Finally, it should be noted that the methods described here provide a general procedure for the generation of alkyl and substituted-alkyl radicals of known structure for examination by e.s.r. spectroscopy, requiring only 0.01-0.05 moles of the appropriate halogeno-compound. They have the virtue, at least in the cases we have described, of giving only one radical, and thus facilitating spectral interpretation. This is in contrast to the rather unselective methods which have been used previously; for example, the allvl radical is the sole species detected under our conditions whereas when it was previously generated, by the bombardment of cyclopropane with high-energy electrons, it was accompanied by methyl, isopropyl, and cyclopropyl radicals.¹³ Moreover, the experiments we have described concerning the reducing characteristics of the radical •CMe2•OH indicate the possibility of employing this type of system to study both the relative reducing capacities of various organic radicals for a particular halogeno-compound and the relative ease of reductive elimination from various halogenocompounds by a particular organic radical.

EXPERIMENTAL

A Varian e.s.r. spectrometer, with 100 KHz modulation and an X-band Klystron, was used in conjunction with one of three mixing chambers; the first allowed the mixing of two reactants ca. 0.02 sec. before the solution entered the cavity of the spectrometer,⁹ the second (of basically similar design) allowed the mixing of three reactants at the same point, and the third allowed one reactant to be introduced between the mixing point for the first two reactants and the point of entry into the cavity.¹ Splitting constants were measured to within ± 0.1 Oe with the Varian 'Fieldial' magnetic field regulator, both directly and by comparison with a solution of Fremy's salt in water (a_N , 13.09 Oe). g-Factors were measured to within ± 0.0001 by attaching a capillary tube containing an aqueous solution of Fremy's salt (g, 2.0055) to the aqueous sample cell.

3-Iodopropionic acid was prepared by heating a solution of 3-bromopropionic acid (30 g.) and sodium iodide (35 g.) in acetone (50 ml.) at the reflux temperature for 6 hr. The mixture was diluted with water and the ether extract was washed with aqueous sodium thiosulphate and with water and was evaporated. The residual iodo-acid was used without further purification. 2-Iodoethanol was prepared by treating 2-chloroethanol with sodium iodide in acetone,¹⁴ and 3-iodopropanol was likewise obtained from 3-chloropropanol. All other materials were commercial samples.

Typical experiments for reaction in weakly basic conditions were conducted with the first mixing chamber, as follows. (a) The reactant solutions contained: (i) 12.5%(w/v) titanium(III) chloride solution (10 ml./l.), disodium ethylenediaminetetra-acetate (6 g./l.), sodium formate (20 g./l.), and the appropriate amount of potassium carbonate to give pH 8; and (ii) 100-volume hydrogen peroxide (0.8 ml./l.) and the halogeno-compound (2 g./l.). When the halogenocompound contained a carboxylic acid group, the latter solution was also buffered to pH 8 with potassium carbonate. (b) The former solution contained formic acid (17 ml./l.)instead of sodium formate, and ammonia ($d \ 0.880$) was added, instead of potassium carbonate, to give a solution of pH 8. For reduction in acidic conditions, the reactant solutions contained: (i) 12.5% (w/v) titanous chloride solution (10 ml./l.), concentrated sulphuric acid (3.3 ml./l.), and formic acid (13 ml./l.); and (ii) 100-volume hydrogen peroxide (0.8 ml./l.), formic acid (13 ml./l.), and the halogenocompound (2 g./l.).

The following compounds were treated in weakly basic conditions according to method (a): methyl iodide, ethyl iodide (saturated solution), ethyl bromide (saturated solution), allyl bromide (saturated solution), 2-iodoethanol, 3-iodopropanol, 2-bromopropionic acid, bromosuccinic acid, chloral hydrate, p-iodobenzoic acid, chloroacetic acid, dichloroacetic acid, and trichloroacetic acid. The following were treated in weakly basic conditions according to method (b): bromoacetic acid, 2-bromopropionic acid, 2-bromo-2-methylpropionic acid, 3-iodopropionic acid, and 2-bromobutyric acid. The following were treated in acidic conditions: bromoacetic acid, 2-bromopropionic acid, 2-bromobutyric acid, bromosuccinic acid, 2-iodoethanol, trichloroacetic acid, and chloral hydrate. Experiments with the other two mixing chambers were carried out similarly, except that the halogeno-compound and hydrogen peroxide were contained separately, the solution of the former being buffered when necessary.

Reduction in acidic conditions was also carried out with isopropyl alcohol (17 ml./l.) in place of formic acid.

¹⁴ H. Wieland and E. Sakellarios, Ber., 1920, 53, 201.

Bromoacetic acid gave the same spectrum when a solution of the acid (3 g./l.) was added at the second mixing point as when it was contained in the peroxidic reactant for reduction in basic conditions according to method (a). Likewise, it gave the same spectrum when a solution of the acid (2 g./l.)was added at the second mixing point as when it was contained in the peroxidic reactant for reduction in acidic conditions, whether the reductant was derived from formic acid or from isopropyl alcohol (17 ml./l.). In another experiment with isopropyl alcohol to provide the reductant, maleic acid (2 g./l.) was included with the bromoacetic acid added at the second mixing point.

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