cules at ~315 and ~365 cm^{-1}. The peaks of the sharp bands at ~315 cm^{-1} are associated with values of $|\Delta_z| \sim 1 \times 10^{-3}$, and the peaks of the broad bands at ~365 cm^{-1} with values of $|\Delta_z| \sim 0.5 \times 10^{-3}$. The (+) and (−) enantiomers give mirror-image couplets. The CID's of the alcohol (+) and (−) enantiomers have the same signs as the corresponding amine enantiomers. No significant Raman CID was detected in any other band.

We used a Coderg Model PH1 Raman spectrometer equipped for photon counting and a Coherent Radiation Laboratories Model 52A argon ion laser set at 4880 Å. The polarization of the incident laser beam was modulated directly between right and left circular at 90 Hz with a KDP crystal driven by an appropriate square-wave alternating voltage; square-wave modulation can, in principle, eliminate the spurious contributions to I_z arising from the term dependent on θ, η, and P since this term no longer contributes. The component of the Raman light modulated at 90 Hz was the difference in the Raman intensity in right and left circularly polarized light. The noise level of the phase-sensitive detection system corresponded to a value of $\Delta \sim \pm 2 \times 10^{-4}$. The component of the light scattered at 90° and linearly polarized parallel to the scattering plane was sampled since, as stated above, only this component was free from spurious contributions in our instrument.

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L. D. Barron,* M. P. Bogaard, A. D. Buckingham
Department of Theoretical Chemistry
University Chemical Laboratory
Cambridge, England
Received August 17, 1972

Electron Spin Resonance and Electronic Structure of Organic Radicals Containing α-Bromine Atoms

Sir:

Despite the fact that a very wide range of organic radicals have been studied by esr spectroscopy, both in solution and in the solid state, very few have been interpreted for $R_2\dot{C}X$ radicals, where X = Cl, Br, or I. Recently, various $R_2\dot{C}Cl$ radicals have been detected in the liquid state[1] and this has enabled others[2] to interpret esr spectra for such radicals in the solid state that had previously defied complete interpretation.[3] Very recently, a full analysis of the radical $F\dot{C}(CONH_2)Cl$ has been described[4] formed in γ-irradiated $FCH(CONH_2)Cl$ crystals.[5]

Although $H_2\dot{C}Br$ radicals have been matrix isolated and studied by infrared spectroscopy,[6] we know of only one tentative esr identification, in which a multiline esr spectrum for an irradiated single crystal of bromoacetic acid was obtained but was not analyzed.[7] The results reported are of little diagnostic value and, indeed, need not have been due to an α-bromo radical.

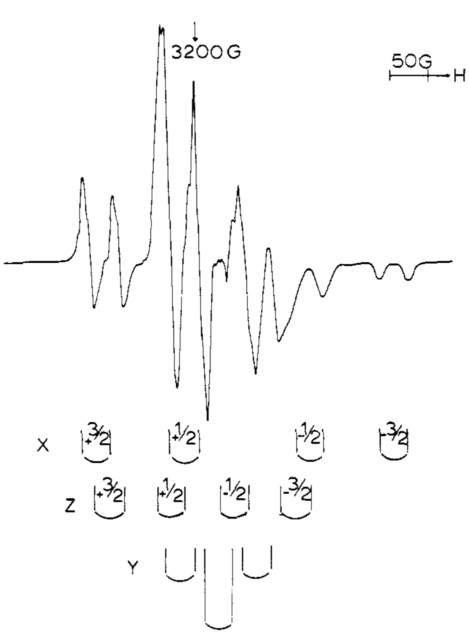

Figure 1. First derivative esr spectrum for powdered α-bromomaleic acid after exposure to ^{60}Co γ-rays at 300 K. This spectrum, especially the features marked A_z, is completely characteristic of $R_2\dot{C}Br$ radicals and can be taken as being diagnostic of their formation.

We have studied a wide range of aliphatic bromides after exposure to ^{60}Co γ-rays at 77 K and have obtained esr spectra which are clearly characteristic of $R_2\dot{C}Br$ radicals. A typical spectrum is given in Figure 1, and such a spectrum may be taken as diagnostic of the formation of such radicals.

In order to proceed with a proper analysis of these spectra, we began by studying the X-band and Q-band powder spectra of typical α-chloro radicals, especially that of $H\dot{C}(CO_2H)Cl$ formed from chloroacetic acid by γ irradiation. Our results (Table I) compare very well with those from single crystals and give us confidence in our procedure.

Analysis of spectra such as that in Figure 1 [for $Br\dot{C}CO_2H(CH_2CO_2H)$] was helped by the following observations. There is a clear set of four doublets (marked A_z). The doublet of *ca.* 40 G stems from hyperfine coupling to one of the β protons and should be nearly isotropic. The quartet is unequally spaced in a manner characteristic of a nuclear quadrupole effect with the magnetic field perpendicular to the major electric field gradient (in this case, the C–Br bond direction). We conclude that this corresponds to a direction perpendicular to the radical plane.[8] Then we expect to find a set of four evenly spaced lines with a high g value for the magnetic field parallel to the C–Br bond (z) and a multiplet at intermediate g values whose form depends upon the relative magnitudes of the hyperfine coupling and $^1/_2e^2Qq_z$, the quadrupole interaction term. The value of $^1/_2e^2Qq_z$ is expected to be close to that for normal C–Br bonds which usually fall close to 80 G.[9] Thus the A_z features

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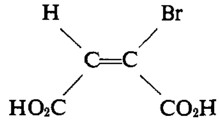
Table I. Esr Data for Various α-Chloro and α-Bromo Radicals Formed in Irradiated Solids

Host	Radical	Hyperfine tensor components, G		g-Tensor components
		^1H	^{35}Cl or ^{81}Br	
$FCH(CONH_2)Cl$[a]	$F\dot{C}(CONH_2)Cl$		18, −3.2, −5.8	2.0021, 2.0069, 2.0076
$ClCH_2CO_2H$	$Cl\dot{C}HCO_2H$	−19, −13, −28	21, −3, −6[b]	2.002, 2.007, 2.009
CH_3Br (in CD_3OD)	$H_2\dot{C}Br$	−21	85	2.002
$BrCH_2CO_2H$	$Br\dot{C}HCO_2H$	−20, −15, −25	107, −48, −75	2.002, 2.016, 2.038
$BrCHMeCO_2H$	$Br\dot{C}MeCO_2H$	22	95	2.002
	$Br\dot{C}CO_2H(CH_2CO_2H)$	38 and <5 (2 H)	111, −50, −80[c]	2.002, 2.018, 2.032[d]
CH_3CH_2Br (in CD_3OD)	$Me\dot{C}HBr$	−22 (1 H), +22 (3 H)	85	2.002

[a] Reference 4. [b] $A_{iso} = +4$ G, $2B_{ax}(x) = +16$ G, $2B_{ax}(z) = -2$G $[a_{p_x}^2 = 16\%, a_{p_z}^2 = -2.0\%]$. [c] $A_{iso} = -6.3$ G, $2B_{ax}(x) = 107.3$ G, $2B_{ax}(z) = -20$ G $[a_{p_x}^2 \approx 19\%, a_{p_z}^2 \approx -3.5\%]$. [d] Orbital magnetism has not been allowed for in the calculations in footnote *c*, but this will not make an appreciable difference to these approximate results.

are nearly normal, but the A_y features are calculated to be a triplet, as shown, together with weak side lines which were not detected. The resulting interpretation, given in Figure 1, was confirmed by Q-band spectra and selected single-crystal studies and is probably fairly accurate.

We have analyzed these results using the signs indicated in Table I, since they give very reasonable results which compare well with those for the α-chloro radicals, whereas any other sign combination gave physically unreasonable results. The main cause of the marked deviation from axial symmetry in the hyperfine tensor components arises because the major spin density is on carbon and so there is a large spin polarization term which contributes negative spin density on bromine. We have, therefore, analyzed the data in terms of two axially symmetric tensors, one parallel to x $[2B_{ax}x]$ (positive) and the other parallel to z $[2B_{ax}z]$ (negative). The results were then converted into approximate orbital populations in the normal manner.[10] In Table I we list the results for the radical from α-bromomaleic acid since this had the most resolved spectrum.

Interestingly, delocalization appears to be slightly larger than that for chlorine which is in accord with the lower electronegativity of bromine. In both cases A_{iso} corresponds to extremely small s-orbital spin densities. This is because the negative contribution from spin on carbon almost exactly cancels the positive contribution from spin on halogen. We conclude that there is appreciable π bonding in agreement with the infrared studies.[6]

Finally, we should mention that the results for methyl and ethyl bromide were obtained using CD_3OD as solvent. This gave spectra of just the same form as that shown in Figure 1, whereas the spectra obtained from the pure compounds were quite different. These will be discussed in detail in our full report of this work. The esr spectra for ethyl bromide and α-bromopropionic acid also contained features characteristic of β-bromo radicals,[11] but these are sufficiently different to enable clear identification to be made for both species.

S. P. Mishra, G. W. Neilson, M. C. R. Symons*
Department of Chemistry, The University
Leicester, LE1 7RH, England

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Determination of the Composition and Sequence of a Glucan Containing Mixed Linkages by Carbon-13 Nuclear Magnetic Resonance

Sir:

Although carbon-13 nmr has been applied extensively to monosaccharides[1-3] and oligosaccharides,[3,4] its potential in determining polysaccharide structure has not been explored to any great extent. An investigation of amylose, a simple homopolymer, has been reported,[3] and more recently the ^{13}C spectrum of heparin, a heteropolymer, yielded information from which an alternating sequence of its two different component sugar residues was proposed.[5] We report here an investigation which demonstrates the remarkable resolution and scope of ^{13}C nmr for studies of polysaccharides. Multiplet resonances of conformational origin are present in the spectra.[6] Both the composition and sequence of a glucan (ex. *Tremella mesenterica*, NRRL Y-6158[7]) are obtainable from the ^{13}C nmr spectrum.

Chemical evidence has indicated that the glucan contains two types of linkage, 1 → 4-α and 1 → 6-α, in an approximate ratio of 2:1.[7] Thus, one might expect different ^{13}C resonance frequencies for the various anomeric, four, and six carbon atoms, depending on whether or how they are linked. Examination of the

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