Electron Spin Resonance Spectrum of a Radical Cation of Ethyl Bromide Radiolytically Produced in Trichlorofluoromethane at 4 K: a Re-investigation

Martyn C. R. Symons *
Department of Chemistry, The University, Leicester LE1 7RH
Hachizo Muto, Kazumi Toriyama, Keichi Nunome, and Machio Iwasaki *
Government Industrial Research Institute, Nagoya, Hirate, Kita, Nagoya 462, Japan

Exposure of a dilute solution of ethyl bromide in $CFCl_3$ to *X*-rays at 4 K gave a species exhibiting a large hyperfine coupling to bromine, with smaller splittings from one chlorine nucleus and two protons. Computer simulations of this well resolved spectrum showed that the *g* tensor is rhombic with the principal elements typical of π^3 radicals. The species is now unequivocally identified as the cation of ethyl bromide having a weak σ^* bond to a single chlorine atom of a neighbouring solvent molecule. The *g* tensor is used to show the relationship between $EtBr^{+\bullet}$ and the isostructural π^3 radicals $RO^\bullet$, $RS^\bullet$, and $CH_3I^{+\bullet}$

It has recently been suggested that the radical cations of various alkyl chlorides and bromides formed radiolytically in trichlorofluoromethane ($CFCl_3$) form weak σ-bonds to one chlorine ligand of a neighbouring solvent molecule.[1] However, the spectra were poorly defined except for the parallel (*z*) features; in addition, the axially symmetric *g* tensor with $g_\perp \gg g_\parallel$ was unreasonably assumed in the spectral analysis, since such a *g* tensor cannot be assigned to $RX^{+\bullet}$. Nor can such behaviour be assigned to $RX^{+\bullet}$---ClR, for which we expect $g_\parallel \gg g_\perp$, theoretically[2] and by analogy with results for isostructural π^3 radicals such as $RO^\bullet$ (ref. 3) and $RS^\bullet$ (ref. 4) (Table).

Far better defined spectra have now been obtained for ethyl bromide cations in $CFCl_3$ by working at 4 K (Figure 1), and attempts have been made to obtain good simulated spectra using a rhombic *g* tensor, in which g_{int} is closer to g_{min} rather that to g_{max}. We have managed to obtain a good simulation [Figure 2(a)] using the data given in the Table; the previously reported *g* tensor[1] does not reveal the observed spectrum at all [Figure 2(b)]. Although the g_{int} value is somewhat larger than that expected by comparison with $RO^\bullet$ and $RS^\bullet$,[3,4] the *g* tensor can be reasonably assigned to $RX^{+\bullet}$, which forms a weak σ-bond with neighbouring Cl. The relatively large g_{int} value probably arises because of the large spin–orbit coupling for bromine.

These results show conclusively that the SOMO for these radicals is strongly localized on bromine, the spin-density, estimated in the usual way from the ^{81}Br hyperfine tensor components, being *ca.* 89%.[2] Clearly the *g* tensor is governed by spin-density on bromine, the degeneracy of the π-levels being lifted by interaction with the surroundings, including weak bonding to chlorine.

It is interesting that there is a marked change in the e.s.r. parameters after annealing to 77 K and recooling to 4 K (Table). Most noteworthy is the large reduction in g_{max} from 2.490 to 2.393. This implies an increase in the interaction with the environment including the strength of the σ-bond, presumably resulting from relaxation of the matrix such that optimum bonding could be achieved. Changes in the hyperfine coupling constants cannot be used directly to assess spin-density changes, because orbital magnetic contributions have also changed. However, it is clear that there are no major changes in electron distribution.

The large *g* anisotropy of this species may be compared with that of $CH_3I^{+\bullet}$ in $CFCl_3$ previously studied.[1] The value of the *g* shift, Δg_{max} ($= g_{max} - g_f$), is approximately proportional to the spin-density (ρ) on the halogen atom and to the spin–orbit coupling constant (ξ), giving the relation (1), where ΔE is the

$$\frac{\Delta g_{max}(Br)}{\Delta g_{max}(I)} = \frac{\rho_{Br}\cdot\xi_{Br}/\Delta E_{Br}}{\rho_I\cdot\xi_I/\Delta E_I} \qquad (1)$$

crystalline field splitting of the degenerate non-bonding orbitals in the free state. Using $\rho_{Br} = 0.89$ and $\rho_I = 1.0$ together with the spin–orbit coupling constants of Br (2 460 cm^{-1}) and I (5 060 cm^{-1}) atoms,[2] $\rho_{Br}\cdot\xi_{Br}/\rho_I\cdot\xi_I$ is obtained as 0.43, in good agreement with the observed *g* shift ratio of 0.36. The results indicate that

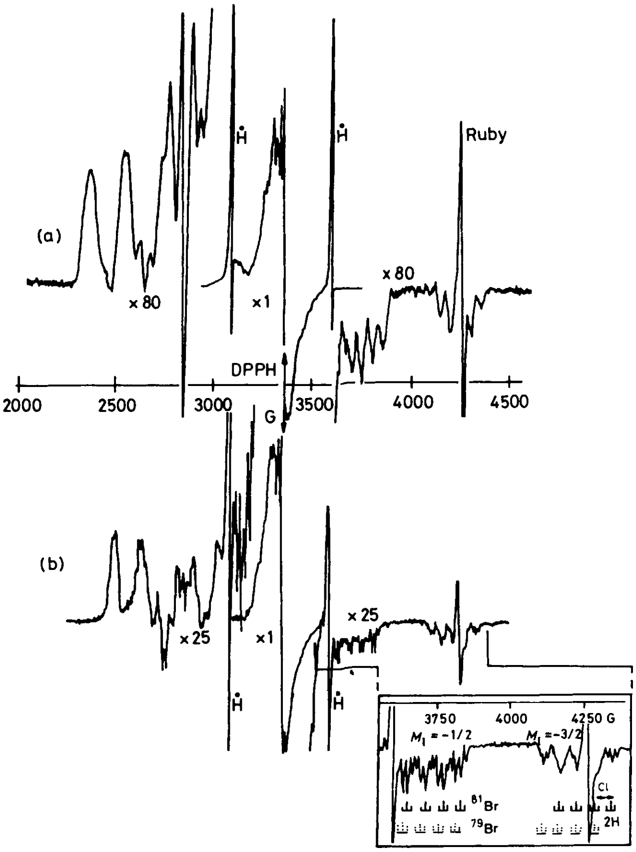

Figure 1. Observed e.s.r. spectra of the radical cation of ethyl bromide radiolytically produced in $CFCl_3$ at 4 K: (a) measured at 4 K immediately after irradiation at 4 K; (b) measured at 4 K after annealing at 77 K [inset in Figure 1(b) shows an enlargement of the proton hyperfine substructures]

Table. Values of the *g* and hyperfine coupling tensors of radical cations of ethyl bromide and methyl iodide radiolytically produced in $CFCl_3$. The *g* tensors of $RO^{\bullet}$- and $RS^{\bullet}$-type radicals are also indicated for comparison

Radicals	Irradiation temperature (K) (measured)	*g* Tensor			Hyperfine tensor[b]				
		g_{xx}	g_{yy}	g_{zz}	Nucleus	$A_{\parallel}$	$A_{\perp}$	eQq[c]	Ref.
$C_2H_5Br^{+\bullet}$---$ClCFCl_2$	77	2.392	2.392	1.922	^{79}Br	464	159	500	1
	(77)				^{81}Br	500	171	420	
					^{35}Cl	57	*ca.* 17		
$C_2H_5Br^{+\bullet}$---$ClCFCl_2$	4.2	2.490	2.10	1.902	^{81}Br	490	200	420	*a*
	(4.2)				^{35}Cl	53	18		
	4.2 [77][d]	2.392	2.08	1.922	^{81}Br	500	171	420	*a*
	(4.2)				^{35}Cl	57	17		
CH_3I^+	77	3.61	1.2	0.85	^{127}I	550			1
$RO^{\bullet}$[e]	4—77	2.076	2.006	1.998					3
$RS^{\bullet}$[f]	77	2.066	2.010	2.000					4
	(180)								

[a] Present work. [b] $1G = 10^{-4}$ T. [c] MHz. [d] After annealing at 77 K. [e] Averaged value from a number of substituted alkoxyl radicals. [f] The sulphur-centred radical formed in irradiated L-cystine dihydrochloride.

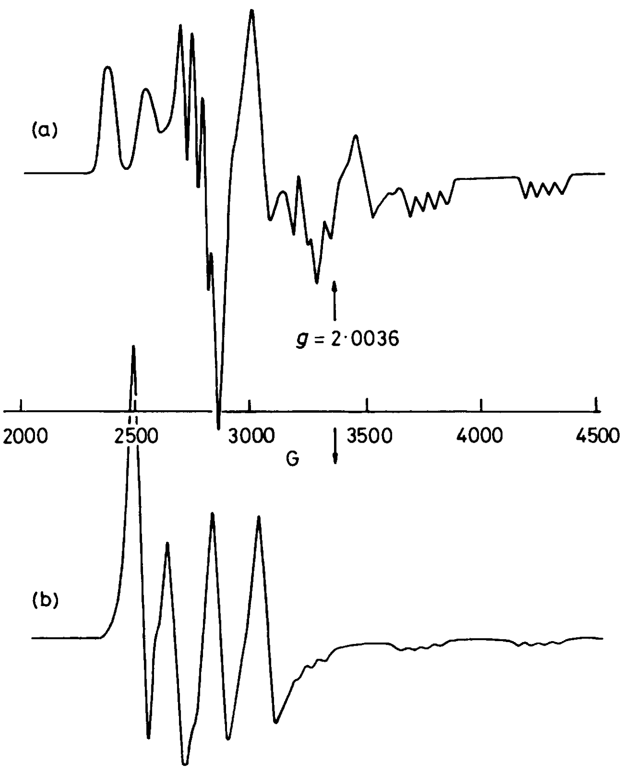

Figure 2. Simulated e.s.r. spectra of the radical cation of ethyl bromide assuming (a) rhombic *g* tensor given in the Table for the case immediately after irradiation at 4 K; (b) axially symmetric *g* tensor given in the Table for the case of irradiation at 77 K

the crystalline field splittings of the two species are not very different. This is an important result since no chlorine hyperfine coupling was resolved in the spectra of $CH_3I^{+\bullet}$, so the source of the required splitting (ΔE = 18 kcal mol) was unknown. This result suggests that it is still caused by weak bonding to chlorine.

We have also found that the Cl substructure is further split into 1:2:1 triplets (*ca.* 15 G splitting), which are reasonably ascribable to the methylene protons in the ethyl group [see Figure 1(b)]. This result provides firm evidence for the assignment to the parent cation of EtBr. It also shows that delocalization onto the alkyl group is quite small.

Finally, we refer to a previous suggestion[1] that $EtBr^{+\bullet}$ may have properties in common with a species formed in irradiated *N*-bromosuccinimide, which was described as a bromine atom formed from the parent cation.[5] There seemed to be no clear reason why the parent cation should decompose to give $Br^{\bullet}$; it was therefore suggested that this species might, in fact, be the parent cation rather than a bromine atom.

However, this comparison was based on the mistaken approximation that the *g*-tensor for $EtBr^{+\bullet}$ was axial, with $g_{\perp} \gg g_{\parallel}$. The present results show that this is not the case; hence the analogy breaks down. Furthermore, unpublished results[6] suggest that the parent cations of *N*-bromosuccinimide and related imides do not resemble this species nor do they appear to break down by the suggested pathway.[5] We conclude that the 'bromine-atom' description is reasonable but that its mechanism of formation is unclear.

Experimental

Dilute solutions of EtBr in $CFCl_3$ (Tokyo Kasei) were irradiated with an *X*-ray source at 4 K. E.s.r. spectra were recorded directly with a Bruker ER-200D spectrometer at 4 K and also after annealing to 77 K and recooling to 4 K.

Spectral simulations were carried out with a FACOM M340S computer by use of the second-order solution of the general spin Hamiltonian in an arbitrary co-ordinate system including the quadrupole term derived by one of us[7] and programmed by Shimokoshi.[8]

References

1 G. W. Eastland, S. P. Maj, M. C. R. Symons, A. Hasegawa, C. Glidewell, M. Hayashi, and T. Wakabayashi, *J. Chem. Soc., Perkin Trans. 2*, 1984, 1439.
2 For example, P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967.
3 W. A. Bernhard, D. M. Close, J. Hüttermann, and H. Zehner, *J. Chem. Phys.*, 1977, **67**, 1211.
4 K. Akasaka, S.-I. Ohnishi, T. Suita, and I. Nitta, *J. Chem. Phys.*, 1964, **40**, 3110.
5 H. Muto and L. D. Kispert, *J. Chem. Phys.*, 1980, **72**, 2300.
6 M. C. R. Symons, unpublished work.
7 M. Iwasaki, *J. Magn. Reson.*, 1974, **16**, 417.
8 F. Shimokoshi, unpublished work.

Received 7th March 1986; *Paper* 6/462