Possible Electron Spin Resonance Identification of Br^{2-} and I^{2-} in γ-Irradiated Bromide or Iodide Doped Barium Sulphate

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Summary Radical species showing strong hyperfine coupling to one bromine or iodine nucleus detected in γ-irradiated barium sulphate doped with bromide or iodide are identified as the species Br^{2-} and I^{2-}, respectively.

BARIUM SULPHATE, precipitated from aqueous solutions containing bromide or iodide ions, incorporates these ions, presumably into sulphate sites. (This was established by diffuse reflectance u.v. spectroscopy). On exposure to ^{60}Co γ-rays at 77 K, in addition to the normal radical products, species characterised by hyperfine coupling to either one bromine or one iodine nucleus were obtained. In both cases the lines were almost isotropic with a very large splitting and low g-value (see Table). We tentatively postulate that the species concerned comprise electrons trapped at the bromide or iodide sites, and are therefore conveniently describable as Br^{2-} and I^{2-}.

Unfortunately we are not able to use the isotropic hyperfine coupling constants to calculate good values for the spin densities since we do not have values for the appropriate outer s-orbitals. Furthermore allowance must be made for the di-negative charge and, especially for iodine, a relativistic correction is necessary.[1] A very rough computation suggests values in the region of 50% for the spin density in both cases. These ions are of interest because of their relationship to the excited states of halide ions in crystals and in solution. The results confirm that the involvement of outer s-orbitals in the excited states is considerable, which would appear to support a confined model.[2]

Species of this type have previously been invoked to explain the marked broadening and the negative g-shift which occur when alkali metal halides, especially iodide, are added to metal–ammonia solutions.[3] Taking the present g-values as limiting, we calculate that about a 5% conversion would account for the maximum shifts detected.[3]

E.s.r. parameters for the Br^{2-} *and* I^{2-} *radicals in barium sulphate*

Radical	g^a	$A(G)^a$
Br^{2-}	1·972	449 (^{81}Br)
	1·970	420 (^{79}Br)
I^{2-}	1·804	924

^{a} Calculated using the Breit–Rabi equation.

However, a species originally thought to be F^{2-}[4] is now known to be better described as the unit Be_2F^{2+}.[5,6] It seems that in this case the σ^* levels are lower than the $3s$ fluorine orbital. Whilst it is reasonable that structures of this type make some contribution in our case, they are less likely to be of major significance since barium is not normally covalently bound and the outer s-orbitals for bromide and iodide are far more available than is that for fluoride.

If this postulate is correct then we must conclude that electron trapping by anions can compete with electron trapping by cations. The species I^{2-} and Ba^+ are isoelectric and one might have expected the latter to be favoured over the former. However, the environment of I^- is far more favourable for trapping than is that for Ba^{2+}. The same conclusion was drawn from our metal–ammonia results.[3]

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[1] J. H. Mackey and D. F. Wood, *J. Chem. Phys.*, 1970, **52**, 4914.

[2] T. R. Griffiths and M. C. R. Symons, *Trans. Faraday Soc.*, 1960, **56**, 1125.

[3] R. Catterall and M. C. R. Symons, *J. Chem. Soc.*, 1964, 4342.

[4] L. Novak, Z. Sroubek, and K. Zdansky, *Phys. Status Solidi*, 1964, **6**, 173.

[5] H. J. Bower, M. C. R. Symons, and D. J. A. Tinling, "Radical Ions," eds. E. T. Kaiser and L. Kevan, Interscience, London, 1968.

[6] T. L. Estle and A. R. Reinberg, *Phys. Rev.*, 1967, **160**, 263.