Electron Spin Resonance Studies of Metal–Metal and Metal–Halogen Bonding in Manganese Carbonyls

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Summary E.s.r. spectra of γ-irradiated $Mn_2(CO)_{10}$ and $Mn(CO)_5Br$ at 77K are shown to be characteristic of the corresponding radical anions, having their unpaired electrons largely confined to σ^* Mn–Mn and Mn–Br bonds, respectively.

PARAMAGNETIC organometallic complexes are rare.[1,2] We have used the technique of solid-state γ-irradiation at low temperatures to produce new paramagnetic species from decacarbonyldimanganese, $Mn_2(CO)_{10}$, and bromopentacarbonylmanganese (I), $Mn(CO)_5Br$.

The e.s.r. spectrum of the product on γ-irradiation of pure powdered $Mn_2(CO)_{10}$ at 77K is characteristic of a species containing two magnetically equivalent manganese atoms and one unpaired electron. This species, which has g-tensor components close to the free-spin value, exhibits an axial spectrum, with the parallel and perpendicular features each split into eleven lines by the two equivalent manganese nuclei. The splittings measured from the spectrum are $A_{\parallel} = 34{\cdot}9$ and $A_{\perp} = 29{\cdot}2$ G. Although the signs of the hyperfine tensor components are not established, the most chemically reasonable combination of signs is for $A_{\parallel}$ to be positive and $A_{\perp}$ negative, in which case $A_{\text{iso}} = -7{\cdot}8$ and $2B = +42{\cdot}7$ G. These values, together with the theoretical values for Mn^0,[3] give approximately 50% $3d$ population on each manganese nucleus. A small but significant population of the $4s$ orbital (*ca.* 1·5%) is necessary to accommodate the value of A_{iso} obtained.

The excess electron is thus interpreted as occupying the antibonding σ^* orbital formed mainly from the two metal $3d_{z^2}$ atomic orbitals. The small $4s$ admixture serves to reduce the antibonding effect with respect to the manganese interaction.

The e.s.r. spectrum of the product on γ-irradiation of pure $Mn(CO)_5Br$ powder at 77K is also axial, with $g_{\parallel}$ and $g_{\perp}$ again close to the free-spin value. The main hyperfine splitting is provided by bromine, with the parallel and perpendicular features due to manganese occurring as splittings on the parallel and perpendicular bromine lines (Figure). The isotopic features from ^{79}Br and ^{81}Br are clearly resolved, the parameters measured from the spec-

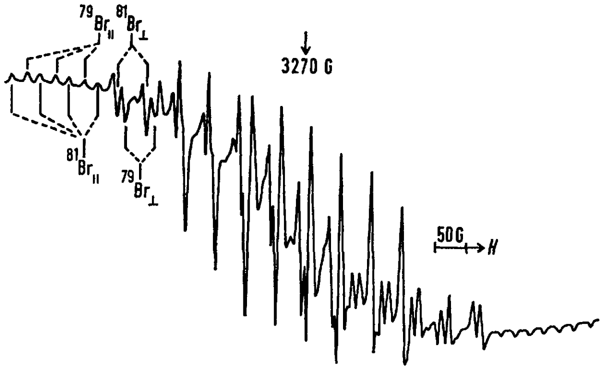

FIGURE. *First derivative e.s.r. spectrum for* $Mn(CO)_5Br$ *after exposure to* ^{60}Co *γ-rays at* 77K.

trum being $A_{\parallel}$ (Mn) $= \pm 48$, $A_{\perp}$ (Mn) $= \pm 50$; $A_{\parallel}$ (^{81}Br) $= 240$, $A_{\perp}$ (^{81}Br) $= 119$; and $A_{\parallel}$ (^{79}Br) $= 222$, $A_{\perp}$ (^{79}Br) $=$ 110 G. Again, orbital symmetry and chemical considerations make the contribution of $A_{\parallel}$ (Mn) positive and $A_{\perp}$ (Mn) negative appear most likely, in which case A_{iso} (Mn) $= -17$ and $2B$(Mn) $= 65$ G. Comparison with the e.s.r. data for Br_2^- [4] and related species enables a choice of sign to be made for the bromine hyperfine tensor components (both positive) and leads to A_{iso} (^{81}Br) $= +159$ and $2B$ (^{81}Br) $= +80$ G, with corresponding figures for the ^{79}Br hyperfine components. These values, combined with the theoretical values for bromine,[5] yield approximately 77% $3d_{z^2}$ and 2% $4s$ population on manganese, and 2% $4s$ and 16% $4p_z$ population on bromine, accounting for 97% of the spin in the paramagnetic ion. The excess electron is again interpreted as occupying the antibonding σ^* orbital formed from the manganese $3d_{z^2}$ and bromine $4p_z$ orbitals, with small admixtures of $4s$ character in each case. The very small deviations from the free-spin g-value show that the σ^* level is well removed from neighbouring magnetically coupled levels, which is most unusual for transition metal complexes.

In most studies of complexes containing halide ligands it is found that the halogen atomic orbital π-levels are considerably below the metal d-levels, and hence that σ- or π-delocalisation is small. However, in a recent study of the photoelectron spectra of various pentacarbonylmanganese derivatives,[6] including $Mn(CO)_5Br$, it has been demonstrated that the sequence of filled levels must be $8e > 7e > 2b_2$, where the outermost level, $8e$, is strongly localised on the halide ion. Fenske and DeKock[7] have concluded that this sequence of levels requires that the halogen π levels have nearly the same energy as those of the metal $3d$ (π) levels. That this is to be expected for these carbonyls is supported by their LCAO calculations.[7]

Our results also support these conclusions. The magnitude of the hyperfine coupling to the bromine nuclei, and the derived spin-density on bromine are very much greater than any values previously reported for halide complexes and the estimated electron distribution could only occur if the degree of covalency is high.

The photoelectron spectra and their assignments,[6] together with the calculations,[7] also strongly support our contention that the centres under consideration are the anions rather than the cations of the parent molecules.

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