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Preliminary communication

DEFINITIVE EVIDENCE THAT THE ESR SPECTRUM OBSERVED DURING PHOTOLYSIS OF $Mn_2(CO)_{10}$ IN THF IS DUE TO OCTAHEDRAL HIGH-SPIN (d^5) MANGANESE(II)

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Summary

The reassignment to a manganese(0) quartet state by C.L. Kwan and J.K. Kochi (J. Organometal. Chem., 101 (1975) C9) of the ESR spectrum obtained during photolysis of $Mn_2(CO)_{10}$ in THF is shown to be in error; computer simulation of the X-band spectrum and observation of the S-band spectrum confirm our previous assignment to sextet manganese(II) and chemical and IR evidence indicate the presence of $[Mn(CO)_5]^-$ as a counter ion.

The nature of the species responsible for the ESR spectrum observed during the photolysis of $Mn_2(CO)_{10}$ in THF [1] is still the subject of controversy. Some of us [2] have recently proposed that a disproportionation of the carbonyl occurs and have argued that a manganese(II) species gives rise to the ESR signal. This point of view has been disputed by Kwan and Kochi [3] who reassigned the spectrum to a quartet state consistent with manganese(0). We consider their reasons for this assignment are based on too simple an interpretation of what is a complicated ESR spectrum and now present further evidence which establishes beyond reasonable doubt that, as we proposed previously, the spectrum is due to manganese(II) in a sextet state. We first discuss the spectroscopic and then the chemical evidence.

It is well-recognised that the hyperfine lines of high-spin manganese(II) in fluid solution are inhomogeneously broadened because the large ^{55}Mn hyperfine interaction removes the degeneracy of the five allowed electron spin transitions [4].

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This gives rise to a characteristic variation in line amplitude; in the X-band ESR spectrum the fourth line from low field is the sharpest and most intense. The linewidths are generally too large for the fine structure to be resolved. However, the species observed in THF has unusually narrow lines and does show fine structure; three components are clearly discernible on the low field line (Fig. 1). The fact that only three, rather than five, components were resolved led Kwan and Kochi [3] to suggest that a quartet, rather than a sextet, state was involved. They attempted to verify this assertion by a computer simulation of the $m_I = 5/2$ and $3/2$ hyperfine lines which showed that five lines should be seen on the outer line for $S = 5/2$, but only three for $S = 3/2$. Unfortunately their theoretical analysis and computer simulation were inadequate in a number of respects. Firstly the transition frequencies were calculated using a second-order expression which did not allow for the variation in magnetic field across the spectrum. Thus, their expression predicts similar fine structure for lines with the same value of $|m_I|$ which is clearly not the case. Secondly, and more seriously, they assumed equal widths for the fine structure transitions, whereas relaxation theory applied to sextet or quartet spin states predicts different widths [5]. In fact the outer $\pm 5/2 \leftrightarrow \pm 3/2$ transitions have the greatest width which is why they are not resolved. We were therefore not convinced by their reassignment of the spectrum and have sought further evidence to resolve the controversy.

Firstly, we have performed a simulation of the X-band spectrum using line positions calculated by exact numerical diagonalisation of the spin Hamiltonian and line widths from the Redfield relaxation matrix. These simulations were carried out in Southampton using the method first described by Luckhurst and Pedulli [6]. It proved possible to account for the temperature variation of the X-band spectrum over a wide temperature range by varying the correlation time for the relaxing dynamic perturbation. A typical simulation and experimental spectrum are shown in Fig. 1. The agreement is excellent; this was also the case for other temperatures.

Secondly, we have obtained the spectrum of the photolysis product at S-band, rather than X-band, microwave frequencies. The operating frequency of the former spectrometer is lower by a factor of three, and the S-band spectrum shows much larger deviations from first-order behaviour. In particular the fine structure transitions are more widely separated and should be better resolved. The low field half of the S-band spectrum, recorded at Leicester, is shown in Fig. 2. The lowest field hyperfine line clearly shows five components confirming that we are observing a sextet, rather than a quartet, state species. The general appearance of the spectrum is very similar to that reported by Burlamacchi [7] who has given a detailed theoretical account of the S-band spectrum of Mn^{2+} in H_2O; our spectrum is better resolved, but otherwise shows the same features. As predicted [7], the fifth line in the spectrum is now the sharpest and least inhomogeneously broadened, whereas the fourth line is sharpest in the X-band spectrum.

As a further argument against manganese(II) being present, Kwan and Kochi [3] observed that the spectrum of manganese(II) perchlorate in THF has broader lines of almost equal amplitude. We have also examined the X-band spectrum of $[Mn(THF)_6]^{2+}$ with $[ClO_4]^-$ as the counterion and agree that the lines are broader. However, we have found that adding tetra-n-butylammonium perchlorate to the photolysis product also leads to line broadening. It thus appears

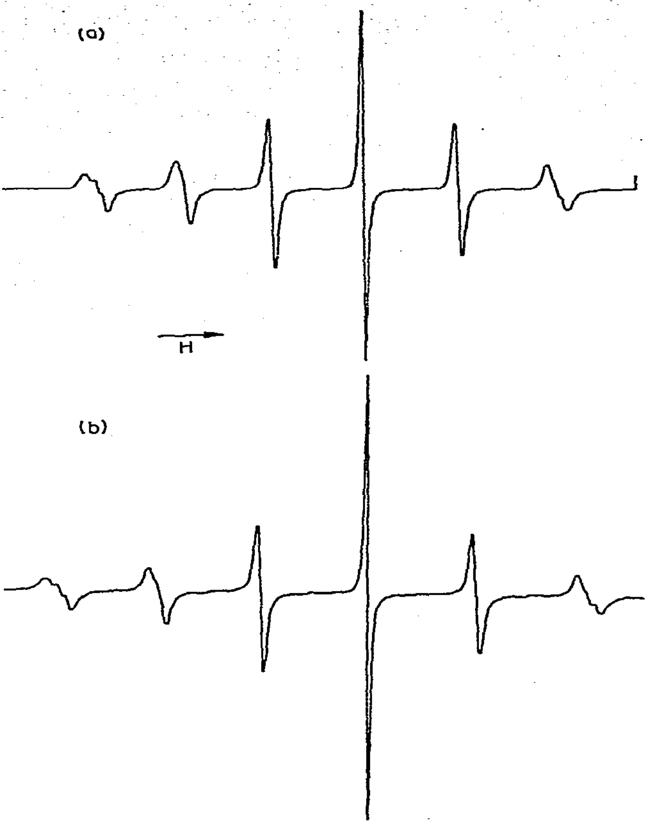

Fig. 1. The X-band ESR spectrum (a) of the photolysis product of $Mn_2(CO)_{10}$ in THF recorded at −18°C. The computer simulation (b) was obtained [6] using a correlation time of 0.35×10^{-12} s and a value of 6×10^4 G^2 for the inner product (D:D), where D is the zero-field splitting tensor.

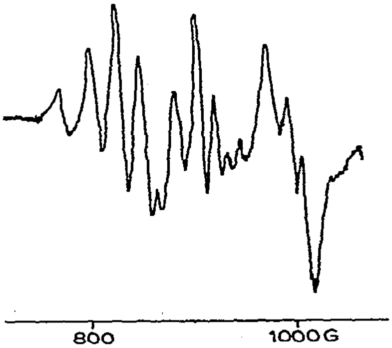

Fig. 2. The low field portion of the S-band spectrum showing fine structure associated with the first three hyperfine lines.

that the presence of $[ClO_4]^-$ affects the line widths (see also ref. 8) more than the counter ion produced in the photolytic disproportionation which we believe to be $[Mn(CO)_5]^-$ (vide infra). Moreover the positions of the sharp lines of the photolysis product are exactly superimposable on those of $[Mn(THF)_6]^{2+}$ from $[Mn(ClO_4)_2]$.

The observation that the photolysis product disappears on introduction of O_2, whereas the spectrum of manganese(II) perchlorate is unaffected, can be accounted for by the presence of $[Mn(CO)_5]^-$. In our original note [2] we wrote the overall reaction as:

$$3[Mn_2(CO)_{10}] + 12S \rightarrow 2[Mn(S)_6]^{2+} + 4[Mn(CO)_5]^- + 10CO$$

The presence of Mn^{2+} would seem to be firmly established, but the case for $Mn(CO)_5^-$ requires further evidence. We have therefore recorded the IR spectrum of a solution of $[Mn_2(CO)_{10}]$ in THF both before and after irradiation at 350 nm; The photolysed solution exhibits new peaks at 1898 and 1863 cm^{-1} which are also present in the literature spectrum of $[Mn(CO)_5]^-$ [9]. We also note that base-induced disproportionation is well-established for a number of metal carbonyls including $Mn_2(CO)_{10}$ [10].

The nature of the solvent appears to be critical in facilitating the disproportionation to manganese(II). Photolysis of $[Mn_2(CO)_{10}]$ in 2-MeTHF, DME, diethyl ether, or tetrahydropyran does not give rise to the sharp six line ESR spectrum found in THF; However, we have recently found that a six line spectrum, albeit with slightly broader lines, can be detected when trimethylene oxide is used as a solvent. Formation of a precipitate was also observed and we associate this with nucleophilic attack by $[Mn(CO)_5]^-$ on the strained four-membered ring.

Acknowledgements

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