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Preliminary communication

REASSIGNMENT TO A MANGANESE(II) SPECIES OF AN ESR SPECTRUM ATTRIBUTED TO $Mn(CO)_5$

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Summary

The ESR spectrum observed during photolysis of $Mn_2(CO)_{10}$ in THF is due to Mn^{II}, not to $Mn(CO)_5$.

There is much current interest in the reactions and spectroscopic properties of the manganese pentacarbonyl radical. Spin-trapping coupled with ESR spectroscopy has indicated formation of $Mn(CO)_5$ during photolysis of a number of its acyl and alkyl derivatives [1] in accord with chemical evidence. Recent matrix isolation IR work suggests that the radical has a square pyramidal geometry [2]. There have been two reports of ESR spectra attributed to $Mn(CO)_5$ but one of these was later shown to be due to $(CO)_5MnOO$ [3]. Photolysis of a solution of $Mn_2(CO)_{10}$ at 350 nm in THF gives a six line ESR spectrum, with $a(^{55}Mn) = 93$ G and g close to free spin, attributed by Hallock and Wojcicki [4] to $Mn(CO)_5$. We shall show that the ESR spectrum observed is actually due to a Mn^{II} species which is of interest because of its remarkably narrow hyperfine lines.

Irradiation at 350 nm of a thoroughly dried and degassed solution of $Mn_2(CO)_{10}$ in THF within the cavity of a Varian E3 spectrometer gives at room temperature the spectrum shown in Fig. 1. The signal is not immediately detectable but is easily observed after prolonged photolysis (2 h) and the signal is not changed after the compound is sealed in a tube for several months.

As previously reported [4] the original yellow solution becomes orange during UV irradiation. However, although some fading was apparent our sample was still orange after six months and gave an undiminished ESR signal whereas Hallock and Wojcicki reported both the colour and ESR signal faded with time.

The trace in Fig. 1 is similar in appearance to the spectrum previously assigned to $Mn(CO)_5$ although somewhat better resolved. The hyperfine coupling and g-factor are characteristic of a Mn^{II} species. However, the most noticeable features are the large variation in line amplitude and the appearance

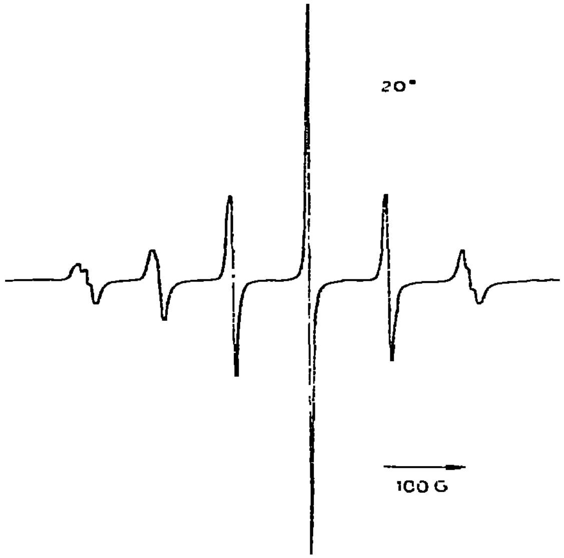

Fig. 1. ESR spectrum of a photolysed solution of $Mn_2(CO)_{10}$ in THF at room temperature.

of fine structure on the outermost lines. It is well known that the hyperfine lines of Mn^{II} are inhomogeneously broadened because the large ^{55}Mn hyperfine interaction removes the degeneracy of the five allowed electron spin transitions [5]. The lines in Fig. 1 are so narrow that the individual transitions are partially resolved. We are not aware of any other Mn^{II} species for which these lines have been resolved in an X-band spectrum: the sharpness of the

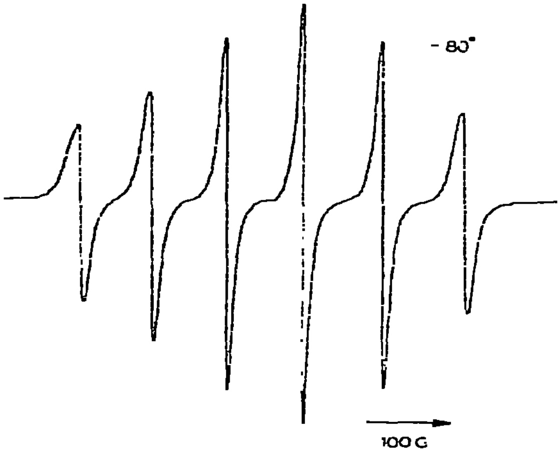

Fig. 2. ESR spectrum of a photolysed solution of $Mn_2(CO)_{10}$ in THF at −80 °C.

lines in Fig. 1 is unprecendented. However, on cooling the lines broaden and at −80 °C (Fig. 2) the spectrum exhibits a more normal appearance. An attempt is underway to account for these line-width variations in terms of appropriate theories of electron spin relaxation [6] and will be reported in due course. Figure 3 shows the ESR spectrum of a frozen solution at −156 °C. It is again characteristic of Mn^{II} in a high spin d^5 configuration with well resolved hyperfine and "forbidden hyperfine" transitions [7].

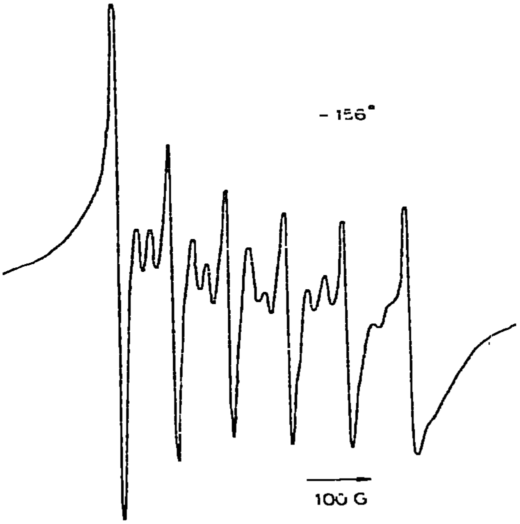

Fig.3. ESR spectrum of a frozen solution of $Mn_2(CO)_{10}$ in THF at −156 °C.

We suggest that the manganese(II) is formed by a photoinduced base disproportionation [8] represented by the overall reaction:

$$3\,Mn_2(CO)_{10} + 12\,S \rightarrow 2\,Mn(S_6)^{2+} + 4\,Mn(CO)_5^{-} + 10\,CO$$

This is supported by the observation that the radical is formed in THF, DME or di-n-butyl ether but not in cyclohexane. The reaction with I_2 to give $IMn(CO)_5$ and the colour changes observed on addition of DPPH* which have been taken as indicating the presence of $Mn(CO)_5$ [4] can equally well be accounted for by the presence of $Mn(CO)_5^{-}$.

We conclude that, although there is good evidence from spin trapping [1] and mechanistic studies that $Mn_2(CO)_{10}$ initially gives $Mn(CO)_5$ radicals on photolysis at 350 nm, the ESR spectrum of manganese pentacarbonyl has not yet been observed. This is probably due to a short radical lifetime and/or broad spectral lines. A slow build up of a stable Mn^{II} species has been demonstrated but the detailed mechanism remains obscure.

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*DPPH = diphenylpicrylhydrazine.

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