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Preliminary communication

ESR SPECTRUM OF MANGANESE SPECIES IN THE PHOTOLYSIS OF $Mn_2(CO)_{10}$ IN SOLUTION

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Summary

The ESR spectrum obtained during the photolysis of $Mn_2(CO)_{10}$ in tetrahydrofuran is assigned to a quartet state consistent with manganese(0), not manganese(II) species; the conclusion is supported by chemical studies.

Photochemical rupture of metal—metal bonded systems represents a potentially valuable method for the generation of transient paramagnetic species. Indeed, there is chemical and physical evidence for the formation of carbonylmanganese(0) during photolysis of decacarbonyldimanganese in solution [1-5]. However, the assignment of the ESR spectrum in Fig. 1 obtained during photolysis of $Mn_2(CO)_{10}$ in tetrahydrofuran (THF) is controversial. The 6-line spectrum showing unusual linewidth effects due to hyperfine splitting by ^{55}Mn was originally observed by Hallock and Wojcicki*. Recently, Hudson, Lappert and Nicholson [5] contended that the spectrum is not due to manganese(0) but to a manganese(II) species formed by disproportionation of $Mn_2(CO)_{10}$. Their argument was based primarily on the stability of the spectrum over a long period (unexpected for a mononuclear manganese(0) species)**, and the spectrum of a frozen solution similar to that of manganese(II) in a high spin d^5 configuration. We wish to present spectral and chemical evidence which does not support the manganese(II) assignment but favors a manganese(0) species.

A 10^{-2} *M* solution of freshly sublimed $Mn_2(CO)_{10}$ in very dry THF*** afforded the ESR spectrum in Fig. 1 immediately upon irradiation with ultraviolet light through a pyrex filter at room temperature. The intensity of

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[*] These authors alluded to $Mn(CO)_5$ as being responsible for the spectrum but did not make the assignment explicitly.

[**] A stable paramagnetic di-1,3-butadienecarbonylmanganese has recently been isolated and its crystal structure determined [6].

[***] THF was refluxed over sodium hydride and stored over Na/K alloy before distilling directly into the ESR tube in vacuo.

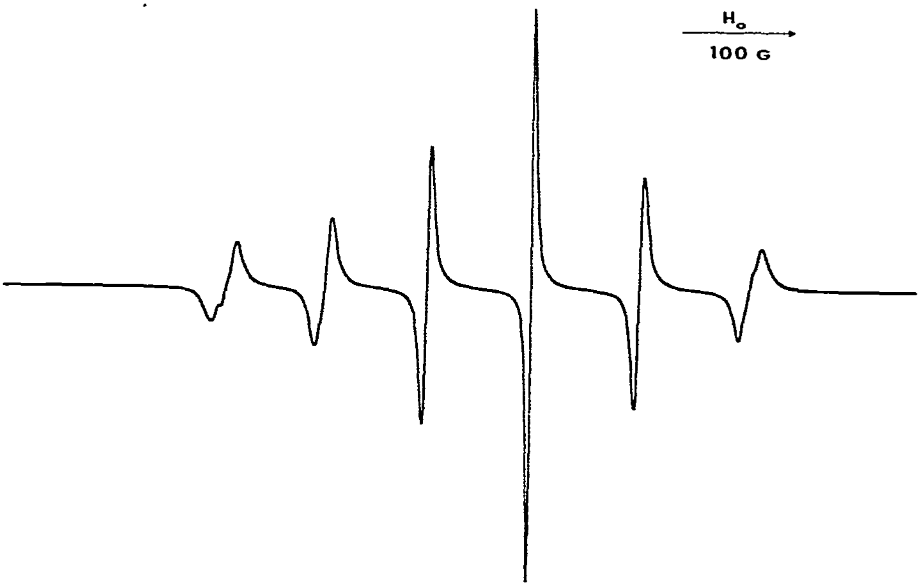

Fig. 1. ESR spectrum obtained from a photolyzed solution of $Mn_2(CO)_{10}$ in tetrahydrofuran at room temperature.

the signal increased rapidly at first, but it reached a plateau after 30 min irradiation*. The light orange solution became wine-red after photolysis at −70°C; and it gradually turned orange then yellow on sitting in the dark at room temperature for a day. The amplitude of the ESR spectrum did not change materially during this period and is, thus, largely independent of these color changes**.

The paramagnetic species responsible for the spectrum is rather stable and a properly sealed solution showed an undiminished signal over a period of a month or more. However, upon introduction of oxygen the spectrum disappeared entirely and the yellow solution turned brown [7]. Removal of oxygen by a thorough degas in vacuo did not restore either the signal or the color. The addition of iodine (via a breakseal) into the photolyzed solution of $Mn_2(CO)_{10}$ in THF caused a marked decrease in the ESR signal. None of these chemical changes could be induced in a THF solution of anhydrous manganese(II) perchlorate [8].

The spin state of the paramagnetic manganese species can be obtained from the observation in Fig. 1 of the broad outer lines with fine structure, in contrast to the narrower central lines showing no further splitting. Using isotropic g and A tensors for the Hamiltonian of the system***, the energy can be calculated to second order by the perturbation method. We find the frequency for the transition between $|M_S, m_I>$ and $|M_{S+1}, m_I>$ to be given

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[*] This observation differs from that of Hudson et al. who reported a 2 h induction period.

[**] The gradual fading of the color which propagated from the surface to the bottom of the solution suggests that it is associated with a diamagnetic species formed by loss of CO (compare ref. 1).

[***] Zero-field splitting, being a traceless tensor, is expected to give no contribution to the Hamiltonian when the paramagnetic species is tumbling fast in solution (see ref. 12).

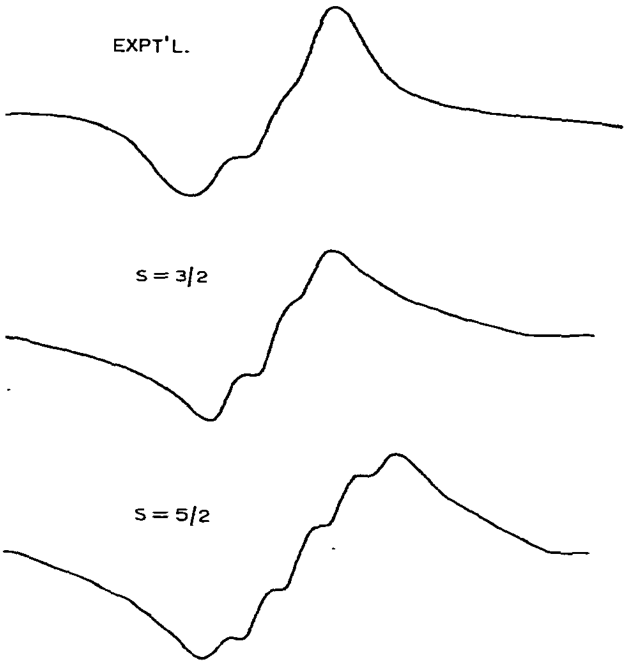

Fig.2. Resolved outer line corresponding to $m_I = 5/2$ of Fig.1. Upper: Experimental spectrum; middle: Computer simulation for $S = 3/2$ using lines with intensity ratios 3:4:3; lower: Computer simulation for $S = 5/2$ using lines with intensity ratios of 5:8:9:8:5.

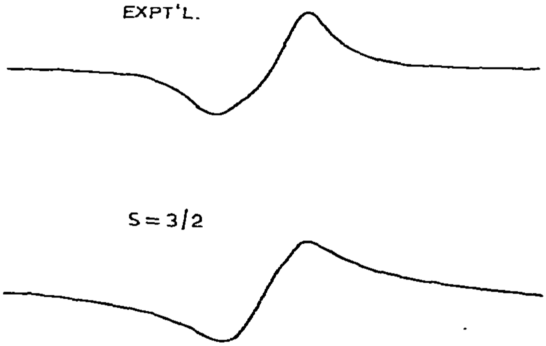

Fig.3. Partially resolved line corresponding to $m_I = 3/2$ of Fig.1. Upper: Experimental spectrum; lower: Computer simulation for $S = 3/2$.

by:

$$h\nu = g\beta H + \left(A + \frac{A^2}{2g\beta H}\right)m_I + \frac{A^2}{2g\beta H}\{I(I+1) - m_I^2\} + M_S m_I \left(\frac{A^2}{g\beta H}\right)$$

where M_S and m_I are the electron spin and nuclear spin magnetic quantum numbers, respectively. The last term is responsible for the fine structure in the spectra. Using $A = 93$ G and $H = 3000$ G, we estimate the splitting between neighboring fine structures to be 7.21, 4.32 and 1.44 for $m_I = \pm 5/2, \pm 3/2$ and $\pm 1/2$, respectively. Close examination of the outermost lines ($m_I = \pm 5/2$)

shows the presence of three lines separated by approximately 7 G [Fig. 2a] which strongly suggests a quartet state. Computer simulation [Fig. 2b] using Lorentzian lines with a half-width of 8.5 G, separation of 7.3 G and intensity ratio 3:4:3 confirms our suspicions that $S = 3/2$, and not 5/2 as shown in Fig. 2c. Computer simulation of the second line of the spectrum in Fig. 3b using a theoretically predicted value for the separation (4.3 G) and a pertinent half-width (8.5 G), also shows that fine structures in the central lines would not be resolved due to their separations being smaller than the linewidths.

We have confirmed [5] the ESR spectrum of a frozen THF solution of photolyzed $Mn_2(CO)_{10}$ showing well-resolved hyperfine splittings in addition to lines due to the so-called forbidden transitions (i.e., $\Delta m_I = \pm 1$). However, the latter are not an exclusive property of sextet states [present, e.g., in high spin manganese(II)]. According to Bleaney and Rubins [9], the forbidden transitions arise from second order effects due to the cross terms in the spin Hamiltonian between the zero field splitting D and the hyperfine splitting A; it is only necessary that $S > 1$. A quartet state for a carbonylmanganese(0) species could certainly account for the frozen spectrum*. On the other hand, a manganese(II) species consisting of a d^5 system in an octahedral or tetrahedral field would produce either a sextet or a doublet state. A quartet state is possible for manganese(II) in a square planar environment, but in searching the literature we could find only two such examples, manganese(II) phthalocyanine and dithiocarbamate [11]. However, in neither case is an ESR spectrum observed in solution due to the highly anisotropic g and A tensors expected for such configurations.

Finally, we have examined directly the ESR spectrum of managense(II) in THF solutions in the presence of the poorly coordinating perchlorate counterion [8]. The spectrum due to $Mn(THF)_6{}^{2+}$ consists of 6 broader lines of almost equal intensity. It is obviously different from that in Fig. 1 but closely resembles the spectrum of $Mn(NCCH_3)_6{}^{2+}$ [12]. The spectrum is unaffected by iodine or by the presence of an oxygen or a carbon monoxide atmosphere.

We conclude that manganese(II) species cannot be responsible for the ESR spectrum of photolyzed $Mn_2(CO)_{10}$. A manganese(0) species as originally proposed [1] is consistent with our results. Unfortunately, more structural information on the manganese(0) species from the hyperfine splittings was not possible due to our inability to observe ^{13}C or ^{31}P (from $Mn_2(CO)_8(PPh_3)_2$) splittings. Studies of the temperature dependence of the line broadening and solvent variation indicate a solvated species**.

Acknowledgement

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[*] A d^7 system in a tetrahedral field could be in a quartet state and have isotropic g and A tensors, an obvious candidate being $Mn(CO)_4$. Depending on the magnitude of the pairing energy, 5-coordinate manganese(0) species in different configurations can also have quartet ground states. For theoretical calculations of various metal carbonyl fragments see ref. 11.

[**] Details of the interesting line broadening and the frozen spectrum will be published separately.

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