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PARAMAGNETIC ORGANOMETALLIC MOLECULES

III *. PHOTOLYSIS OF DIMANGANESE DECACARBONYL

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Summary

The photolysis of $Mn_2(CO)_{10}$ has been investigated over a range of solvents and temperatures and found to be more complicated than hitherto reported. Homolysis of the metal—metal bond in $Mn_2(CO)_{10}$ is the dominant photochemical process in all solvents as evidenced by trapping the $Mn(CO)_5^{\cdot}$ radical. A temperature dependent bifunctionality of the spin-trap 2,4,6-tri-t-butylnitrosobenzene was observed. The unstable adduct $Mn(CO)_5O_2^{\cdot}$, previously characterised in the solid state, is formed in non-polar solvents in the absence of a trap. A paramagnetic species giving rise to a broad, structureless signal at ambient temperatures is the major product in basic solvents; in certain polar solvents at low temperatures, hyperfine coupling to manganese (A(Mn) 88 G) could be distinguished. Both spectra are believed to derive from the solvated manganese(II) ion.

The controversial six-line spectrum found on photolysis of $Mn_2(CO)_{10}$ in tetrahydrofuran also results from a manganese(II) species. The unusual properties of the $Mn_2(CO)_{10}$/THF system may be explained in terms of ion-pair formation between the Mn^{2+} and $Mn(CO)_5^-$ ions in solution.

Introduction

Since the initial observation [2] of a six-line ESR spectrum, produced during the photolysis of a solution of dimanganese decacarbonyl, $Mn_2(CO)_{10}$, in tetrahydrofuran, THF, there has been considerable debate as to the nature of the paramagnetic species. Hallock and Wojcicki [2] attributed the signal to the $Mn(CO)_5^{\cdot}$ radical but this assignment was challenged [3] on the grounds that the line-shape and magnitude of the hyperfine coupling constant ($A(Mn) = 90$ G) were indicative of a metal ion with a high spin d^5 configuration. It was proposed that

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the $Mn(CO)_5^{\cdot}$ radical, which can be trapped in chlorinated solvents [3] and THF [4], disproportionates to manganese(II) and $Mn(CO)_5^-$ in THF. However, the species observed in THF has unusually narrow hyperfine lines for high-spin manganese(II), three components being discernible on the low-field line, and this led Kwan and Kochi [5] to reassign the spectrum to a quartet state consistent with manganese(O). The most recent contribution [6], from workers in three laboratories, refutes Kochi's assignment and offers overwhelming evidence in favour of a manganese(II) species. Base-induced disproportionation is preparatively well established for both thermal [7] and photochemical [8] reactions of $Mn_2(CO)_{10}$.

Kinetic [9] and flash photolysis [10] studies in various solvents support the idea that homolytic cleavage of the Mn—Mn bond is the principal photolysis reaction for $Mn_2(CO)_{10}$ although the lifetime of the $Mn(CO)_5^{\cdot}$ radical is very short [6] and its ESR spectrum is unlikely to be detected under normal conditions. An ESR spectrum of the $Mn(CO)_5^{\cdot}$ radical has been recorded in an argon matrix by Ozin [11] and it is significant that the appropriate hyperfine coupling parameters [$A(Mn)_\parallel = 65.8$ G, $A(Mn)_\perp = 32.8$ G] differ markedly from those obtained for the product of photolysis in THF or for $O_2Mn(CO)_5^{\cdot}$ [12].

It is the purpose of this paper to point out that the photolysis of $Mn_2(CO)_{10}$ is more complex than hitherto reported and that the behaviour in THF is apparently not representative of that for all basic solvents.

Results

Photolysis in hydrocarbon solvents

Photolysis of $Mn_2(CO)_{10}$ at $\lambda > 376$ nm and 143 K in the non-coordinating solvents, 3-methylpentane, isopentane and methylcyclohexane produced a distinctive six-line spectrum with a manganese hyperfine coupling constant of 12.0 G and $g = 2.016$ (A Fig. 1). The low value of the manganese hyperfine coupling constant, compared with those of other species investigated here (vide infra), suggested considerable delocalisation of unpaired electron density away from the manganese nucleus. No signal is obtained if the solutions are saturated with gaseous CO or N_2 prior to photolysis, whereas the signal is enhanced on saturation with O_2. The signal is lost on warming the system above 173 K. The relatively broad lines of this spectrum suggest a degree of anisotropy for the manganese spin system which could be accounted for by the viscosity of the glass causing significant restriction of the molecular motion.

The ESR parameters for species A are similar, though by no means identical, to the value for $O_2Mn(CO)_5^{\cdot}$ ($A(Mn) = 7.03$ G $g = 2.004$) which was identified previously as a product of the vacuum sublimation of $Mn_2(CO)_{10}$ in the presence of traces of oxygen [12]. More recently, Symons and Zimmerman [13] have shown that environmental effects can result in considerable variation of the g and $A(Co)$ values for $O_2Co(CO)_4^{\cdot}$ and this fact, together with the above observations, point clearly to species A being the adduct $O_2Mn(CO)_5^{\cdot}$, with the unpaired electron largely confined to the two oxygen atoms.

Photolysis in polar solvents other then THF

Photolysis of a rigorously purified sample of $Mn_2(CO)_{10}$ at 293 K in the degassed solvents 2-methyltetrahydrofuran (MTHF), diethyl ether (DEE), furan,

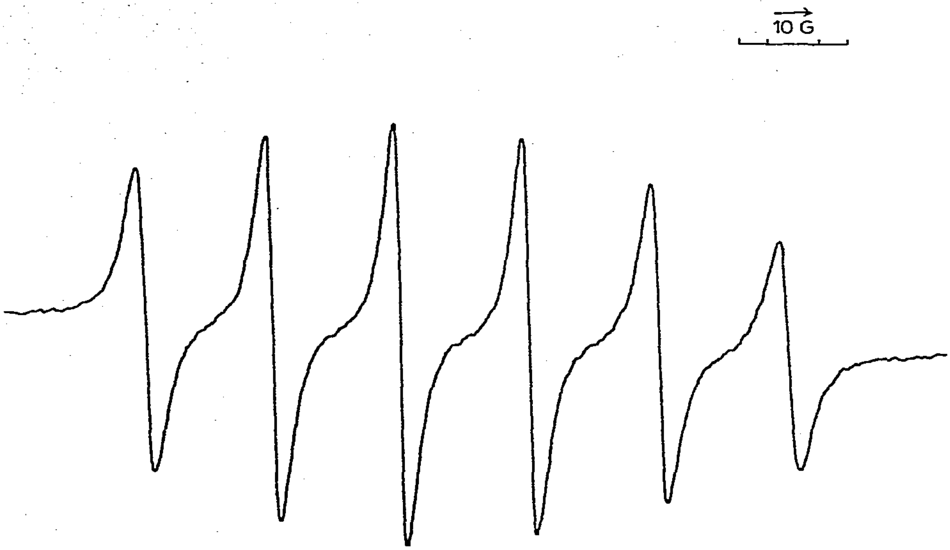


Fig. 1. ESR spectrum of species A, the product of photolysis of $Mn_2(CO)_{10}$ in 3-methylpentane at 143 K: A(Mn) = 12.0 G, g = 2.016.

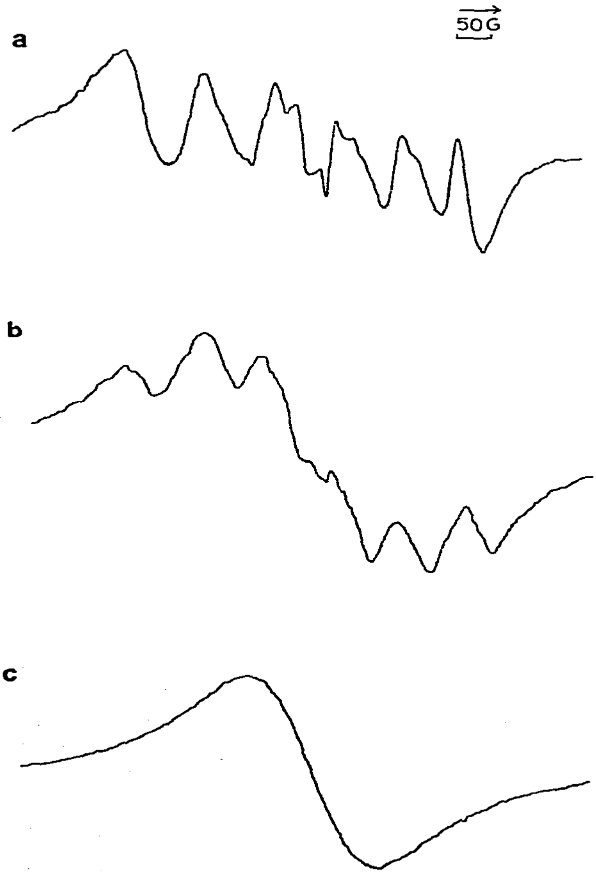


Fig. 2. ESR spectra from the photolysis of $Mn_2(CO)_{10}$ in MTHF. (a) MTHF glass at 143 K: A(Mn) = 88 G, g = 2.005, species C; (b) MTHF at 173 K showing loss of fine structure and growth of species B; (c) MTHF solution at 293 K: g = 2.005, species B.

TABLE 1

EFFECT OF SOLVENTS ON DECOMPOSITION OF $Mn_2(CO)_{10}$

Solvent	$Mn_2(CO)_{10}$ remaining after 1 h photolysis (%)
CH_2Cl_2	93
THF	68
DEE	60
MTHF, DME, TEA	~10

dimethoxyethane (DME), isopropyl alcohol, tetrahydrofuran, triethylamine (TEA) and dichloromethane slowly produced a broad, structureless ESR signal with a g value of 2.005 (B, Fig. 2c), No signal was observed if the solutions were kept in the dark and IR analysis indicated that there was no spontaneous interaction with the solvent. The broad ESR signal must therefore arise from a photochemical reaction of $Mn_2(CO)_{10}$. There is a steady increase in the intensity of this signal as the photolysis proceeds and the signal persisted both when the radiation was removed and when oxygen gas was admitted to the reaction cell. IR analysis of the solutions after 1 h photolysis at 293 K indicated that the decomposition of $Mn_2(CO)_{10}$ (although not necessarily the conversion to B) was more facile in basic solvents.

For donor solvents which do not form glasses, the line shape of the signal due to B is independent of temperature. In contrast, when the photolysis is initiated in a TEA or MTHF glass at 143 K a relatively narrow six-line signal, $A(\text{Mn}) = 88$ G, is slowly formed (C Fig. 2a). The g value for this structured resonance is closely comparable to that observed for B. If the temperature of the system is increased, the manganese hyperfine structure is progressively lost leaving the broad signal, B (Fig. 2b). Reforming the solvent glass in the absence of light does not reconstitute C in either MTHF of TEA. If however the reformed glass is further irradiated, C is again produced, undoubtedly due to further photolytic reaction of the remaining $Mn_2(CO)_{10}$. On this evidence, it would seem reasonable to assign B and C to the same paramagnetic species, the most obvious explanation for this behaviour being a difference in the degree of magnetic dilution achieved in the glass matrix and in solution.

Photolysis in THF

Unlike the photolytic behaviour in other donor solvents, the outcome of photolysis of $Mn_2(CO)_{10}$ in THF is dependent on the concentration of $Mn_2(CO)_{10}$, the intensity of the incident radiation and the purity of the THF. At a $Mn_2(CO)_{10}$ concentration of 1×10^{-1} mol dm^{-3}, photolysis with a 250 W mercury lamp produced a broad ESR signal similar to B, obtained in other polar solvents. If the $Mn_2(CO)_{10}$ concentration is reduced to 1×10^{-2} mol dm^{-3} identical photolysis conditions lead to initial observation of a signal B, which is swamped after 30 min irradiation by the strong six-line spectrum D noted by earlier workers [2—5] (Fig. 3a).

It must be stressed that these results were obtained using the photolysis equipment described in the experimental section. However qualitative experiments, varying the power of the light source and the nature of the optical system

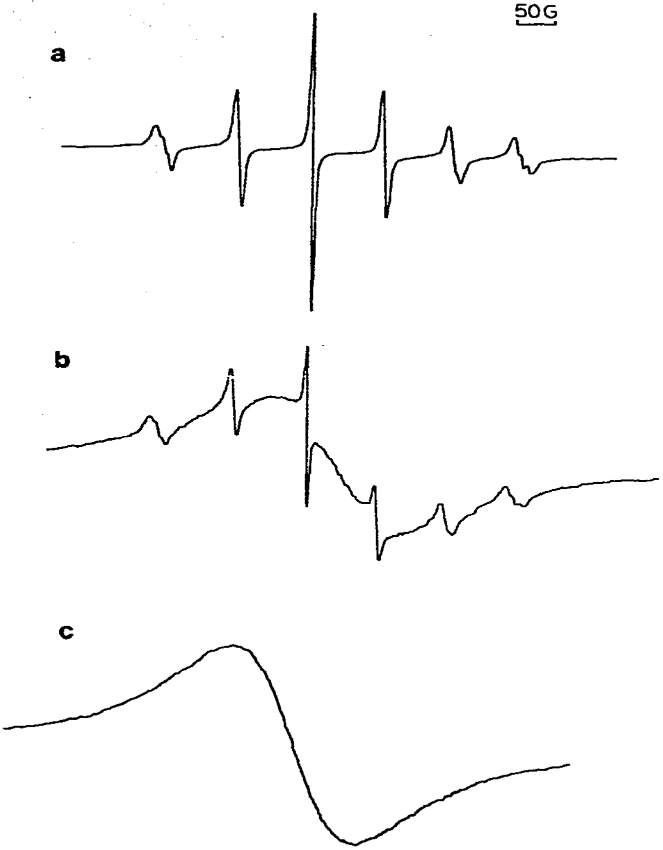


Fig. 3. ESR spectra from the photolysis of $Mn_2(CO)_{10}$ in THF. (a) After 30 min irradiation at 293 K: A(Mn) = 93 G, species D; (b) after 90 min irradiation showing loss of fine structure and growth of species B; (c) after several hours irradiation, g = 2.005.

altered both the induction period for the appearance of D and the extent of decomposition of $Mn_2(CO)_{10}$. This presumably accounts for the failure of other workers to observe signal B. Prolonged photolysis (several hours) of the dilute solutions leads to photo-bleaching of D, leaving signal B; (Fig. 3b, 3c). Similarly, D but not B disappears when the system is exposed to oxygen.

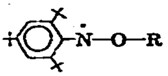
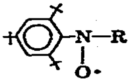
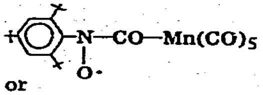
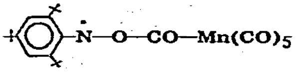
The addition of trace quantities of MTHF to the photolysis system causes the complete collapse of D and indeed numerous other polar solvents have the same effect. Furthermore reversible collapse of the structured signal is observed when THF solutions exhibiting D are warmed beyond 308 K.

Spin-trapping of the $Mn(CO)_5^{\cdot}$ radical

Lappert and coworkers [4,14] have shown that a variety of metal-centred radicals can be trapped using nitrosodurene and in this manner trapped the $Mn(CO)_5^{\cdot}$ radical from $CHCl_3$, CH_2Cl_2 and THF solutions. Using the spin-trap 2,4,6-tri-t-butylnitrosobenzene (TNB) [15] we have independently trapped this radical in all the solvents used in our study with the exception of TEA and i-PrOH

TABLE 2

ESR PARAMETERS ^{a} FOR TRI-t-BUTYLNITROSOBENZENE SPIN-ADDUCTS OF THE PRODUCTS FROM THE PHOTOLYSIS OF $M_2(CO)_{10}$ (M = Mn, Re)

	 (Anilino I)	 (Nitroxide II)	 or  (III) ^{b}
R = Mn(CO)₅			
A(N)/*G*	11.3	13.25	9.00
A(H)/*G* ^{c}	1.7	1.68	1.90
A(Mn)/*G*	3.25	7.15	21.5
T(K)	213	233	293
R = Re(CO)₅			
A(N)/*G*		11.75	
A(H)/*G* ^{c}		1.65	
A(Re)/*G*		12.90	
T(K)		183—293	

[a] In 3-methylpentane solution. [b] Possible formulations of the spin adduct III (see text). [c] *A*(H) refers to coupling to the *meta* hydrogen.

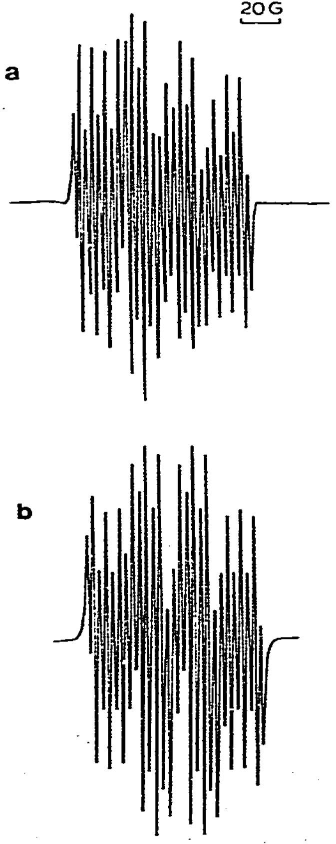


Fig. 4. (a) ESR spectrum of the anilino spin-adduct I, from the photolysis of $Mn_2(CO)_{10}$/TNB in 3-methylpentane at 213 K; (b) simulated spectrum.

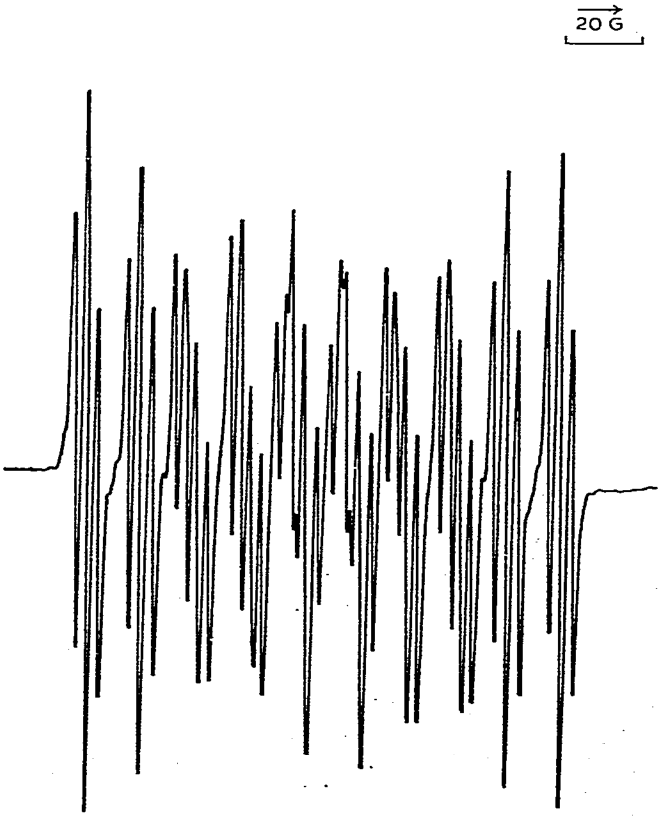


Fig. 5. ESR spectrum of the nitroxide spin-adduct II, from the photolysis of $Mn_2(CO)_{10}$/TNB in 3-methylpentane at 233 K.

which were found to react with the trap. For a normal trapping experiment an excess of the spin-trap was used. No evidence for a trapped dinuclear manganese radical, comparable to that reported by the Sussex group [4,14], was found as the concentration of the spin-trap was varied.

TNB has two potential trapping sites and, depending on their size, alkyl radicals can form either the anilino (I, Table 2), favoured by bulky alkyl radicals, or nitroxide (II, Table 2) spin adducts [14].

Surprisingly, it was possible to distinguish three different spin adducts from the photolysis of $Mn_2(CO)_{10}$ in the presence of TNB. When a solution of $Mn_2(CO)_{10}$ in 3-MP was photolysed at 213 K, the ESR spectrum to first appear (Fig. 4a) had $A(Mn) = 3.25$ G and $A(N) = 11.3$ G. (all spectra were successfully simulated assuming coupling to a single manganese nucleus, e.g. see Fig. 4b). As the photolysis continued, a spectrum due to a second spin adduct emerged with a spectral width exceeding that of the first. This second species was characterised by higher A(Mn) and A(N) values, (Fig. 5). Anilino spin-adducts of TNB typically have lower ^{14}N coupling constants than the corresponding nitroxide species [15] and, on this basis, we assign the first spectrum to that of an anilino spin-adduct (I, $R = Mn(CO)_5$) and the second to the nitroxide (II, $R = Mn(CO)_5$). This assignment is also consistent with a higher spin density on the manganese when bound to the less electronegative nitrogen atom.

There was no apparent increase in the intensity of I during photolysis but the spectrum due to I disappeared entirely on cessation of photolysis whereas that of II remained. Further irradiation of the sample caused the spectrum due to I to reappear. At temperatures above 233 K only the nitroxide adduct II is produced. This novel behaviour indicates that the nitroxide adduct is thermodynamically more stable but that formation of the anilino adduct is kinetically favoured. The formation of nitroxide or anilino spin-adducts with alkyl and aryl radicals is controlled by steric factors, with the anilino form favoured by radicals with the greatest steric requirement [15]. It is of interest to note in this context, that the $Re(CO)_5^{\cdot}$ radical is trapped only as the nitroxide (II, $R = Re(CO)_5$) over the entire temperature range (183–293 K). This observation may reflect the increased radius of the rhenium atom compared to manganese and the preference for coordination by the heavier metal to an element of lower electronegativity (i.e. nitrogen).

Trapping experiments at ambient temperatures (293 K) were complicated in the manganese system by the appearance, on prolonged photolysis, of a further spin adduct, III, (Table 2) characterised by a much higher ^{55}Mn hyperfine coupling constant but a lower value for A(N). In order to account for the increased spin-density on manganese, we tentatively suggest that III is produced by carbonyl insertion into either I or II. No comparable $Re(CO)_5$ spin adduct could be detected which offers indirect support for our formulation of III, since it is well known that carbonyl-insertion reactions are rare in rhenium chemistry [16].

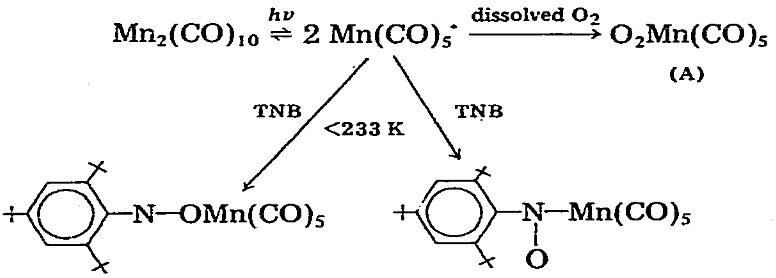
Coupling constants for the nitroxide TNB—$Mn(CO)_5$ (Table 2) spin adducts and those of nitrosodurene [4,14] are, as expected, very similar. No such correlation exists however when the corresponding $Re(CO)_5$ spin adducts are compared. The A(Re) values differ in the two systems by some 28 G. The lower spin density at the rhenium atom for the TNB adduct may reflect a considerable steric interaction between the *ortho*-t-butyl substituents of the spin trap and the $Re(CO)_5$ fragment although it is perhaps surprising that the anilino form is not produced so as to minimise these interactions.

Extremely complex spectra are produced when spin-trapping of the $Mn(CO)_5^{\cdot}$ radical is attempted in THF and MTHF. In addition to the spectra of the $TNBMn(CO)_5$ spin adducts, photolytic cleavage of these solvents gave rise to further spin adduct species [16]. Generally, the spectra are sufficiently well resolved to allow the characterisation of the TNB—$Mn(CO)_5$ moieties but this observation does raise a question as to the role of products of solvent cleavage in the overall photochemical reactions of $Mn_2(CO)_{10}$ (vide infra).

Discussion

There is no doubt that photolysis of $Mn_2(CO)_{10}$ at energies close to the $\sigma \rightarrow \sigma^*$ transition results, for all solvent systems examined here, in homolytic cleavage of the metal—metal bond. (Scheme 1). The $Mn(CO)_5^{\cdot}$ radicals so produced have an extremely short lifetime on the ESR timescale, due either to a rapid recombination reaction ($k(293\ K) = 3.3 \times 10^9\ mol^{-1}\ s^{-1}$) [10] or to a facile interaction with the solvent system. If, as predicted [18], $Mn(CO)_5^{\cdot}$ has square pyramidal geometry then its short lifetime is understandable. The manganese atom in this geometry will be coordinatively unsaturated and will therefore readily coordinate a sixth ligand in the axial position. Oxygen fills this role in the adduct $O_2Mn(CO)_5$ (Scheme 1); the $Mn(CO)_5^{\cdot}$ radicals, once formed, abstract traces of dissolved oxygen from the hydrocarbon solvents to give the paramagnetic adduct (species A). Manganese is also coordinatively saturated in the spin adducts $Mn(CO)_5$—TNB. In these non-polar solvent systems, competition for the vacant manganese coordination site, between the spin-trap species and dissolved oxygen, clearly favours spin adduct formation. At low temperatures, the kinetically favoured anilino derivative is formed with an oxygen donor atom occupying the vacant coordination site. The thermodynamically more stable nitroxide is the sole product at higher temperatures, binding in this instance via the nitrogen atom of the spin-trap molecule.

SCHEME 1

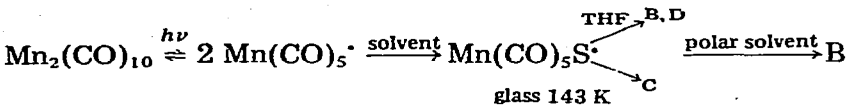


(Anilino, I)

(Nitroxide, II)

The situation in basic solvents is by no means as clear-cut but the overall picture is summarised in Scheme 2.

SCHEME 2



$$Mn_2(CO)_{10} \overset{h\nu}{\rightleftharpoons} 2\,Mn(CO)_5^{\cdot} \xrightarrow{\text{solvent}} Mn(CO)_5S^{\cdot} \begin{cases} \xrightarrow{\text{THF}} B, D \\ \xrightarrow[\text{glass 143 K}]{} C \end{cases} \xrightarrow{\text{polar solvent}} B$$

Initial reversible homolytic cleavage of the Mn—Mn bond is followed by coordination of a solvent molecule to give the coordinatively saturated $Mn(CO)_5S^{\cdot}$. The fate of this species is dependent on the solvent and the reaction conditions but there is overwhelming evidence that the final paramagnetic product, in all polar solvent systems, involves manganese(II).

Let us first consider the photolysis in polar solvents other than THF, which can be seen from Scheme 2 to lead to species B or C depending on the reaction conditions. The following facts lead us to believe that both these species involve the high spin $[Mn(S_6)]^{2+}$ cation arising from the disproportionation of the $Mn(CO)_5S^{\cdot}$ according to eq. 1.

$$3\,Mn(CO)_5S^{\cdot} + 3\,S \rightarrow [Mn(S_6)]^{2+} + 2\,Mn(CO)_5^{-} + 5\,CO \qquad (1)$$

1. There is a well established precedent for the disproportionation of $Mn_2(CO)_{10}$ to manganese(II) in basic solvents [7,8]. Furthermore, the counterion $Mn(CO)_5^{-}$ has been identified in the photolysed solutions [6] by the presence of bands at 1898 and 1863 cm^{-1} in the infrared spectra [19]. All attempts to precipitate this ion with heavy cations were however unsuccessful.

2. Species B persists indefinitely if the solutions are exposed to oxygen, as would be expected for solvated manganese(II). C however appears only under certain well defined photolysis conditions which precludes a meaningful investigation of its oxidative stability.

3. The temperature variation of the ESR spectra of manganese(II) in various solvents have been extensively described and analysed [20—22]. The spectrum of species C at 143 K is identical to that reported elsewhere for manganese(II) in, for example, frozen methanol [22] and a Sephadex gel [20]. The absence of hyperfine structure in the spectrum of species C after it had been warmed to 293 K and recooled to 143 K can be explained in a similar manner to that for the slow freezing of aqueous $MnCl_2$ [20]; viz. any hyperfine structure is broadened by dipolar interactions which arise from high "local" concentrations that result from the freezing process. Furthermore, the absence of hyperfine structure in the spectrum of species B at 293 K may be due to a relaxation mechanism related to the solvation of manganese(II) in the form $[MnS_6]^{2+}$. This would cause extensive line broadening and consequent loss of hyperfine structure.

4. For reasons detailed by Lappert et al. [3,6] with which we fully concur, the resolved fine structure of spectra C and D and the corresponding manganese hyperfine coupling constants of ~90 G are entirely consistent with the paramagnetic species being a manganese(II) ion in the sextet state.

5. Plots of signal intensity against time (Fig. 6) show the rate of formation of B to be independent of the $Mn_2(CO)_{10}$ concentration but to depend on the basicity of the solvent and on the temperature. This leads to the conclusion that the disproportionation reaction is the rate determining step in the formation of B.

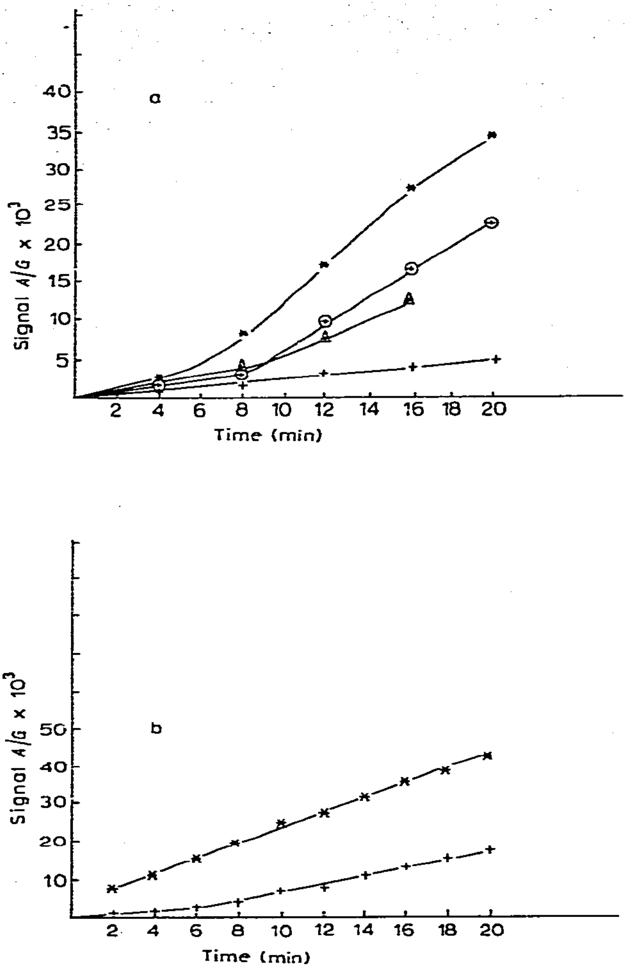


Fig. 6. Plots of signal ($A/G \times 10^3$) with time for the growth of signal B in the photolysis of $Mn_2(CO)_{10}$ in polar solvents. (a) Solvent variation (* diethyl ether, ⊕2-MTHF, △THF, + CH_2Cl_2): (b) temperature variation in MTHF (* 303 K, + 273 K).

A similar investigation of the rates of formation of $TNBMn(CO)_5$ (nitroxide form) reveals that there is no correlation between the formation of the spin adduct and that of B under comparable conditions of temperatures and concentration. It must be acknowledged that such a comparison makes the rather drastic assumption that the rate of $Mn(CO)_5^{\cdot}$ radical formation is unaffected by the spin-trap. With this proviso in mind, these observations lend considerable support to the homolysis/disproportionation pathway outlined in Scheme 2.

6. A striking similarity exists between plots of signal amplitude against time for the formation of B in basic solvents (Fig. 6a) and the rate at which gaseous CO is lost from a solution of $Mn_2(CO)_{10}$ on photolysis [8]. This again suggests that B is formed after Mn—Mn bond cleavage in keeping with the proposed photolysis mechanism.

7. The behaviour of $Re_2(CO)_{10}$ on photolysis is significantly different from

that of $Mn_2(CO)_{10}$. Spin-trapping experiments show that the metal—metal bond is homolytically cleaved under comparable experimental conditions but, in the absence of spin-trap, no paramagnetic species are observed. It would appear therefore that $Re(CO)_5^{\cdot}$ does not disproportionate, an observation that is entirely consistent with the known chemistry of rhenium [16,23]. Obviously in this system, radical recombination is favoured over the disproportionation reaction, even in polar solvents.

Having assigned species B and C to the $[Mn(S_6)]^{2+}$ ion, there remains the problem of identifying the species giving rise to the much debated species D in THF. The work of Lappert et al. [3,6] points clearly to a manganese(II) ion in a high-spin configuration. Nonetheless, the spectrum obtained in THF differs markedly from those of B and C which we believe also to derive from high-spin $[Mn(S_6)]^{2+}$. Before the species can be unequivocally assigned, the following key observations have to be rationalised:

(a) The signal D is unique to THF *.

(b) The paramagnetic species was found to be sensitive to air above 293 K and to temperature above 308 K. When these conditions are met, signal D disappears and only the broad signal B remains.

(c) Addition of trace quantities of another basic solvent (MTHF, DEA etc) to the photolysed solution quenches signal D leaving B.

(d) Photobleaching of D occurs on prolonged photolysis; again signal B remains (Fig. 3b and 3c).

(e) The nature of the counterion has a marked effect on the spectral line-width; for example, a THF solution of $Mn(ClO_4)_2$ exhibits a six-line spectrum but the lines are much broader and of almost equal amplitude. Furthermore, addition of $[Bu_4N][ClO_4]$ to the $Mn_2(CO)_{10}$ photolysis product also leads to broadening of the spectral lines [6].

A possible rationale of the observation of D in THF is that it results from ion association in THF solution leading to the presence of free or solvent separated ions $[Mn(S_6)]^{2+}$ giving rise to a type B signal and contact ion pairs $[Mn]^{2+}$ $[Mn(CO)_5]^-$ or triple ions $[Mn]^{2+}[Mn(CO)_5^-]_2$ which produce the type D signal. The work of Edgell [29—31] has shown that THF encourages ion pair formation involving metal carbonyl anions, an observation in agreement with (a) and (e) above. Furthermore, exposure of the photolysis solution to air or oxygen would result in oxidation of the $Mn(CO)_5^-$ counterion with concomitant loss of the signal due to an ion associated species. The effect [6] of added ClO_4^- on the signal can be rationalised similarly in terms of competition between ClO_4^- and $Mn(CO)_5^-$ ions for intimate association with the paramagnetic cation. Finally, the collapse of signal D at elevated temperatures could result from loss of aggregation as the vibrational energy of the system increases.

Two factors militate against complete acceptance of ion association as a rationale of signal D. The effect of ion association on ESR line widths is well documented [26—28] for manganese(II) in aqueous and alcoholic solutions. In these systems, increasing concentration of a counterion and hence increasing ion association in the solution have the effect of broadening the ESR lines. In

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* The most recent communication from Lappert et al. [6] reports the observation of a six-line spectrum from the photolysis of $Mn_2(CO)_{10}$ in trimethylene oxide. The lines in the spectrum are however much broader than for D.

the system studied here the opposite effect must be implied *. Secondly, photobleaching of the type D signal, which occurs on prolonged photolysis of $Mn_2(CO)_{10}$ in THF, cannot be readily explained in terms of an ion association phenomenon.

An alternative explanation of signal D is that the paramagnetic manganese containing species arises from the $Mn(CO)_5^\cdot$ accelerated photolytic cleavage of the cyclic ether [24]. It is recognised that metal carbonyl species cleave or initiate the polymerisation of THF and the products of such reactions are consistent with the intemediacy of free radicals [25]. Using spin trapping techniques, we have observed the same cleavage products from THF photodegration both in the presence and absence of $Mn_2(CO)_{10}$ [24]. Such an explanation does not however fulfill the requirements of points (a) and (c) in that other ethers are equally photo-active [17].

That the $Mn_2(CO)_{10}$/THF system is a complex one is readily appreciated. Dissociation and subsequent reaction of the $Mn(CO)_5^\cdot$ radical occurs alongside cleavage of the solvent. The fate of the radicals produced from THF cleavage is little understood and it may be that reactions occuring between these and either the manganese(II) cation species or the $Mn(CO)_5^-$ counterion result in the unique behaviour observed in THF solution.

Experimental

Dimanganese decacarbonyl and dirhenium decacarbonyl (Strem Chemicals) were purified by vacuum sublimation and stored in vacuo. The solvents 1,2-dimethoxyethane, tetrahydrofuran and diethyl ether were dried by standard methods, distilled and stored in the presence of the anthracene radical anion. 2-Methyltetrahydrofuran was distilled from sodium to remove the stabiliser and stored, in the dark, over sodium. All other solvents were purified by standard procedures. 2,4,6-Tri-t-butylnitrosobenzene was prepared by the published method [32].

The ESR spectra were recorded with a Varian E4-spectrometer equipped with the Varian V-2507 variable temperature facility. Field linearity was checked with Fremy's salt and the estimated accuracy of hyperfine coupling constants is ±0.02 G. ESR spectra were simulated using the program SIMESR written by one of us (BMP).

Sample preparation prior to photolysis involved the use of normal high vacuum procedures; typically $Mn_2(CO)_{10}$ (0.013 mmol) in 0.6 cm^3 of rigorously degassed solvent was used. Photolysis took place in the spectrometer cavity using a Hytek 250 W ME/D mercury lamp at 376, 405 and 436 nm. The radiation was focussed onto the sample by means of two quartz lenses, one of focal length 12.5 cm, closest to the lamp and the other of focal length 20 cm adjacent to the cavity. Before recording spectra at low temperatures the solutions were individually checked for transparency. In spin trapping experiments the mol ratio of spin-trap to $Mn_2(CO)_{10}$ was maintained at approximately 2 : 1.

For the kinetic experiments samples were prepared as detailed above with the

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* In a separate series of experiments in our laboratories [24] we have found that treatment of a THF solution of anhydrous manganese(II) perchlorate with an excess of $Mn(CO)_5^-$ leads to the loss of the structured six-line signal and the appearance of a broad resonance similar to that of signal B.

$Mn_2(CO)_{10}$/spin-trap ratio held at 2 : 1. Spectra were recorded in 1 min intervals and a plot of signal against time produced, where signal is defined as the ratio A/G (A = signal amplitude, mm; G = receiver gain [33]). All other instrumental settings were held constant throughout the experiment. For measurements in the absence of spin trap, the amplitude of the broad signal B was recorded, while the growth of the nitroxide spin adduct (II) was monitored using the amplitude of the second peak which we adjudged to be the least susceptible to broadening effects.

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References

1 A.M. Bond, B.M. Peake, B.H. Robinson, J. Simpson and D.J. Watson, Inorg. Chem., submitted for publication.
2 S. Hallock and A. Wojcicki, J. Organometal. Chem., 54 (1973) C27.
3 A. Hudson, M.F. Lappert and B.K. Nicholson, J. Organometal. Chem., 92 (1975) C11.
4 A. Hudson, M.F. Lappert, P.W. Lednor and B.K. Nicholson, J. Chem. Soc. Chem. Commun., (1974) 966.
5 C.L. Kwan and J.K. Kochi, J. Organometal. Chem., 101 (1975) C9.
6 A. Hudson, M.F. Lappert, J.J. MacQuitty, B.K. Nicholson, H. Zaimal, G.R. Luckhurst, C. Zannoni, S.W. Bratt and M.C.R. Symons, J. Organometal. Chem., 110 (1976) C5.
7 W. Hieber, W. Beck and G. Zeitler, Angew. Chem., 73 (1961) 364.
8 W. Strohmeier, C. Barbeau and D. van Hobe, Chem. Ber., 96 (1963) 3254.
9 M.S. Wrighton, Chem. Rev., 74 (1974) 401; M.S. Wrighton and D.S. Ginley, J. Amer. Chem. Soc., 97 (1975) 2065; J.F. Fawcett, R.A. Jackson and A. Poe, J. Chem. Soc. Chem. Commun., (1975) 733.
10 J.L. Hughey and T.J. Meyer, Abstracts VIIth Int. Conf. Organometal. Chem., Venice, 1975.
11 G.A. Ozin, personal communication 1975.
12 S.A. Fieldhouse, R.W. Fulham, G.W. Nielson and M.C.R. Symons, J. Chem. Soc., Dalton Trans., (1974) 567.
13 M.C.R. Symons and D.N. Zimmerman, J. Chem. Soc. Dalton Trans., (1975) 1545.
14 A. Hudson, M.F. Lappert and B.K. Nicholson, J. Chem. Soc., Dalton Trans., submitted for publication.
15 S. Terabe and R. Konata, J. Chem. Soc. Perkin II, (1973) 369.
16 H.C. Lewis and B.N. Storhoff, J. Organometal. Chem., 43 (1972) 1.
17 A.R. McIntosh and J.K.S. Wan, Mol. Photochem., 4 (1972) 417.
18 J.K. Burdett, J. Chem. Soc. Faraday Trans., 2, 70 (1974) 1599, Inorg. Chem., 14 (1975) 375.
19 W.F. Edgell, J. Huff, J. Thomas, H. Lehman, C. Angell and G. Asato, J. Amer. Chem. Soc., 82 (1960) 1254.
20 J.S. Leigh and G.H. Reed, J. Phys. Chem., 75 (1971) 1202.
21 L. Burlmacchi, J. Chem. Phys., 55 (1971) 1205.
22 F. Tsay, G.L. Manatt and S.I. Chan, Chem. Phys. Letters, 17 (1972) 223.
23 R. Colton, The Chemistry of Rhenium and Technetium, Interscience, London, (1965).
24 A.S. Huffadine and B.M. Peake, manuscript in preparation.
25 B.K. Nicholson, B.H. Robinson and J. Simpson, J. Organometal. Chem., 66 (1974) C3.
26 B.R. McGarvey, J. Phys. Chem., 61 (1957) 1232.
27 R.G. Hayes and R.J. Myers, J. Chem. Phys., 40 (1964) 877.
28 L. Burlmacchi and E. Tiezzie, J. Phys. Chem., 73 (1969) 1588.
29 W.F. Edgell, J. Lyford, A. Barbetta and C.J. Jose, J. Amer. Chem. Soc., 93 (1971) 6403.
30 W.F. Edgell and J. Lyford, J. Amer. Chem. Soc., 93 (1971) 6407.
31 W.F. Edgell and A. Barbetta, J. Amer. Chem. Soc., 96 (1974) 415.
32 R. Okazaki, J. Hosogai, E. Iwadare, M. Hashimoto and N. Inamoto, Bull. Chem. Soc., Japan, 42 (1969) 3611.
33 W.G. Bryson, D.P. Hubbard, B.M. Peake and J. Simpson, Anal. Chim. Acta, 77 (1975) 107.