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ESR Investigation of Mn Carbonyl Complexes Formed by Reaction of $Mn_2(CO)_{10}$ with Electron Acceptor Molecules

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*The reaction of $Mn_2(CO)_{10}$ with quinones like acenaphthenquinone (ACNQ), 9,10-phenanthrenquinone (PQ) and tetrachloro-*orthobenzoquinone *(*o-*TCBQ) yields paramagnetic adducts which have been investigated by ESR spectroscopy. While the adducts with ACNQ and PQ are obtained in a thermal reaction, the complex having* o-*TCBQ as a ligand requires a photoassisted reaction to be formed. In the photolysis of* o-*TCBQ in benzene three different adducts are formed with one, two and three* o-*TCBQ chelated to the manganese atom. Spin adducts are also formed when $Mn_2(CO)_{10}$ reacts thermally with tetracyanoquinodimethane (TCNQ) and with 2,3-dichloro-5,6-dicyano-*p-*benzoquinone (DDQ) where a coordination of the metal group to a nitrogen atom is preferred.*

Introduction

The homolysis of the Mn–Mn bond in decacarbonyldimanganese $Mn_2(CO)_{10}$ may occur either by photoassisted or thermal reactions which involve electron acceptor molecules (A).

It was suggested that the reaction proceeds via a charge-transfer (CT) process according to the scheme [1]:

$$(CO)_5MnMn(CO)_5 + A \xrightarrow[(\Delta\ \text{or}\ h\nu)]{CT} [(CO)_5MnMn(CO)_5^{+\bullet}A^{-\bullet}] \longrightarrow$$

$$[(CO)_5MnMn(CO)_5^{+\bullet}A^{-\bullet}] \xrightarrow{\text{fast}} [(CO)_5Mn^{\bullet}(CO)_5Mn\text{–}A^{\bullet}]$$

$$[(CO)_5Mn^{\bullet}(CO)_5Mn\text{–}A^{\bullet}] \rightarrow (CO)_5Mn^{\bullet} + (CO)_5Mn\text{–}A^{\bullet}$$

where as a final step the paramagnetic adduct $(CO)_5$-Mn–$A^{\bullet}$ is formed.

Krusic [2] observed the ESR spectrum of the adduct formed by reacting $Mn_2(CO)_{10}$ with tetracyanoethylene (TCNE) in tetrahydrofuran (THF) while Kochi *et al.* [1] recorded the ESR spectrum of the adduct when the acceptor molecule was 9,10-phenanthrenquinone (PQ) in benzene.

In this paper we report results of an ESR investigation on the paramagnetic species which arise by reaction of $Mn_2(CO)_{10}$ with quinones like acenaphthenquinone (ACNQ) and tetrachloro-*ortho*benzoquinone (*o*-TCBQ) in THF and benzene as solvents, and with tetracyanoquinodimethane (TCNQ-h_4 and TCNQ-d_4) which is expected to behave like TCNE. We have also examined 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) which contains carbonyl as well as nitrile groups.

While the *o*-TCBQ adduct necessitates irradiation to be formed the other species we studied were obtained by thermal reaction with $Mn_2(CO)_{10}$. The *o*-TCBQ adduct was also produced thermally following a different reaction route, as we shall see later.

Experimental

$Mn_2(CO)_{10}$ (Fluka), ACNQ, PQ (Fluka) and *o*-TCBQ (Merck) were commercial products which were purified by vacuum sublimation. TCNQ-h_4 and TCNQ-d_4 were kindly supplied by Prof. C. Pecile of this Laboratory. DDQ (Fluka) was recrystallized from chloroform. The solvent THF was purified by distillation over calcium hydride and stored under vacuum over K-anthracenide, while benzene was Merck UVASOL grade dried over calcium hydride. Samples were prepared using standard vacuum techniques. Irradiation was performed with an OSRAM HBO 500 W mercury lamp whose light was filtered with an aqueous solution containing K_2CrO_4 and KOH.

The ESR spectra were recorded with a JEOL JES-PE-3X spectrometer equipped with variable temperature devices.

TABLE I. Hyperfine Coupling Constants (in Gauss) of the Spin Adducts.

Molecule	Solvent	Species	Mn	Additional Ligand h.c.c.
ACNQ	THF	A′	2.28	a_H = 1.34 (triplet); a_H = 1.05 (triplet) a_H = 0.17 (triplet)
PQ	THF	A′	2.74	a_H = 1.75 (quintet); a_H = 0.43 (quintet)
	Benzene	B	5.50[a]	
o-TCBQ	THF	A′	3.91	
	THF	D	5.71	
	Benzene	B	8.78	a_{Cl} = 0.53 (two chlorines)
	Benzene	C	6.87	
	Benzene	D	5.71	
TCNQ-h$_4$	THF	A	1.23	a_{N_1} = 1.77; $a_{N_{2,3}}$ = 1.20; a_{N_4} = 0.85 a_{H_1} = 2.47; $a_{H_{2,3,4}}$ = 0.32
DDQ	THF	A	1.18	a_{N_1} = 1.18[b]; a_{N_2} = 0.84

[a] See reference 1. [b] a_{N_1} h.c.c. is assigned to the nitrogen bonded to the metal group.

Results

The thermal reaction of ACNQ and $Mn_2(CO)_{10}$ in THF yielded a paramagnetic adduct whose ESR spectrum exhibited hyperfine splittings due to three sets of two equivalent protons and a further splitting due to the ^{55}Mn nucleus with a hyperfine coupling constant (h.c.c.) a_{Mn} = 2.28 G. Both proton and manganese h.c.c.s were weakly dependent on the temperature. Since the value of a_{Mn} we measured for the ACNQ adduct was markedly different from that reported by Kochi *et al.* [1] for the 9,10-phenanthrenquinone adduct (5.50 G in benzene), we considered it worthwhile to re-examine the PQ system also in THF. In the latter solvent the PQ adduct formed exhibited a h.c.c. of manganese of 2.74 G, similar to that of the ACNQ adduct, whereas the other h.c.c.s remained very close to those obtained in benzene. Attempts to prepare the ACNQ adduct in benzene failed because of the low solubility of ACNQ.

For *o*-TCBQ, the thermal reaction with $Mn_2(CO)_{10}$ did not occur but when the solution was irradiated with visible light for a few seconds it turned rapidly dark and a spin adduct was formed. We observed different spectral features when the photolysis was carried out in benzene with respect to THF. In the latter case, the first adduct formed has an a_{Mn} of 3.91 G and after prolonged irradiation it was replaced by a new paramagnetic species having a manganese h.c.c. of 5.76 G.

Incidentally, we obtained the same spin adducts when the *o*-TCBQ molecule reacted in THF with $Na^+Mn(CO)_5^-$ prepared by $Mn_2(CO)_{10}$ and metallic sodium. In this case the reaction proceeds via an electron transfer from the $Mn(CO)_5^-$ anion to *o*-TCBQ.

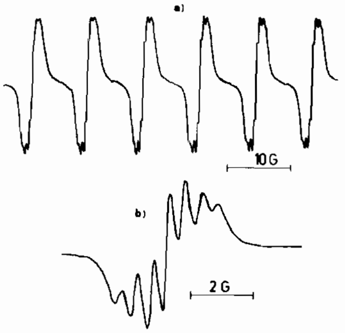


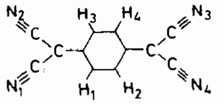
Fig. 1. a) The ESR spectrum of the spin adduct (B) (see text) formed by the photoassisted reaction of *o*-TCBQ with $Mn_2(CO)_{10}$ in benzene. b) The outermost low field component of the spectrum displaying a well resolved hyperfine structure due to two equivalent chlorine nuclei.

In benzene under the same experimental conditions at first an ESR spectrum appeared which displayed the manganese hyperfine coupling constant of 8.78 G and each of the six lines of the spectrum contained an additional hyperfine structure due to two equivalent chlorine nuclei. The spectrum is shown in Fig. 1. As irradiation was continued a new adduct with a_{Mn} = 6.87 G was observed, while the intensity of the primary spectrum was considerably weaker. After a further exposure to the light source the first two species disappeared and another paramagnetic adduct was produced with a value of a_{Mn} = 5.71 G, quite close to that of the final adduct obtained in THF.

It is interesting to note that when the photoassisted reaction is carried out with $Mn_2(CO)_{10}$ in excess with respect to the quinone, the rates of formation of the different adducts changed markedly.

In fact, the primary species with a_{Mn} = 8.78 G lived much longer and the two species having a lower value of a_{Mn} (6.87 G and 5.71 G) are formed only after a prolonged irradiation. The h.c.c.s of the ACNQ, PQ and *o*-TCBQ adducts are collected in Table I.

Paramagnetic adducts were also obtained by reacting in the dark TCNQ (TCNQ-h_4 and TCNQ-d_4) with $Mn_2(CO)_{10}$. The spectrum of the TCNQ-h_4 adduct is exceedingly complex because of the hyperfine splittings due to several unequivalent nuclei. However, it allows the smallest hyperfine couplings due to the ring protons to be determined. The ESR spectrum of TCNQ-d_4 is simpler because three of the four deuterium splittings are too small to be resolved lying within the linewidth (~0.1 G). The spectrum could be computer simulated by the set of hyperfine parameters collected in the Table and the reported h.c.c.s are referred to the nuclei as labelled in the following formula:



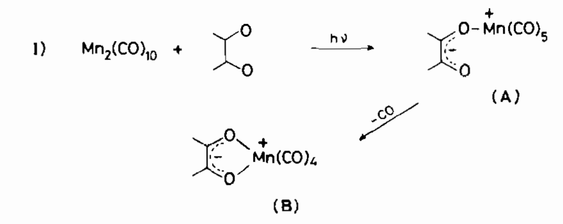
The thermal reaction of $Mn_2(CO)_{10}$ with DDQ yielded a paramagnetic adduct in THF and benzene. The main features of its ESR spectrum were the presence of the manganese h.c.c. and the magnetic unequivalence of the two nitrogen atoms of the DDQ ligand. On passing from benzene to the ethereal solvent we did not note any remarkable change in the h.c.c.s.

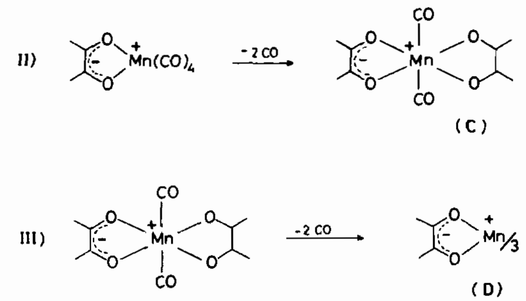
Discussion

As mentioned above, in the reaction of quinones and $Mn_2(CO)_{10}$ the ESR spectrum of the adduct has a value of a_{Mn} which is strongly dependent on the solvent. The occurrence of more than one adduct in the photoassisted reaction of *o*-TCBQ and the appearance of a species having the same value of a_{Mn} in THF and benzene seem to rule out the possibility that the change of a_{Mn} may be merely a solvent effect.

An alternative explanation of such a large variation of a_{Mn} is based on the occurrence of spin adducts having different structures.

A reaction mechanism useful to interpret the photoassisted reaction of $Mn_2(CO)_{10}$ with quinones in solvents like benzene is provided by reactions I, II and III according to the scheme:

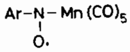




Reaction I was already proposed by Alberti and Camaggi [3, 4].

In thermal reactions of electron acceptor molecules with $Mn_2(CO)_{10}$ it is likely that the initial step in the formation of the spin adduct is a charge-transfer process as proposed by Kochi *et al.* [1]. However, spin trapping and mechanistic studies give evidence that the photolysis of $Mn_2(CO)_{10}$ at 350 nm initially produces $\cdot Mn(CO)_5$ radicals formed by cleavage of the Mn–Mn bond [5]. Thus, in photoassisted reactions that involve $Mn_2(CO)_{10}$ and electron acceptor molecules we cannot exclude that $\cdot Mn(CO)_5$ may be the primary radical and then it transfers an electron to the organic molecule. Anyway, in both reaction pathways the primary *o*-TCBQ adduct formed should be the paramagnetic species designed as (A).

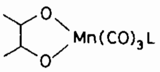
It has been found [5] that spin trapping of $\cdot Mn(CO)_5$ by nitrosodurene yields the trapped nitroxide radical as confirmed by the value of a_N = 15.9 G which is typical for nitroxide radicals with a whole electron on the nitrogen atom. The h.c.c. of manganese was 8.6 G which is of the same order as all the a_{Mn} values measured in the spin adducts we obtained. Therefore the species (A - D) of the reaction scheme must have an even number of electrons, possibly eighteen, in the surrounding of the Mn atom so that the formal oxidation number might be Mn(I).



$$\underset{\substack{|\\ O\cdot}}{Ar-N}-Mn(CO)_5$$

According to the previous scheme the adduct (A) can undergo loss of a carbonyl group bonded to the manganese and thus form the species (B). This process may be favoured by the strong chelating effect which enables the *ortho*quinone radical to be bound to the manganese atom by both oxygen atoms. The observation that the vacuum conditions of the sample were getting worse during reaction, supports the release of a CO molecule. In benzene, while only the adduct (B) was observed with ACNQ and PQ, in the case of *o*-TCBQ at this stage a further irradiation favours the addition of a neutral quinone molecule which replaces two carbon monoxide molecules and the adduct (C) arises. This displacement reaction is possible only when strong π electron acceptor molecules such as *o*-TCBQ are involved [6]. Finally, the species (C) can be converted into the complex (D) by losing two further carbonyl groups. We expect that the a_{Mn} values would be larger in the adduct (B) than in the complexes (C) and (D) where an increased delocalization of the spin density on the quinone molecules and a corresponding reduction of the amount of spin density on the Mn nucleus seem conceivable.

Concerning the structure of the species formed in THF it was observed that the addition of ethers, such as 1,2-dimethoxyethane (DME) to a benzene solution of $Mn_2(CO)_{10}$ and a series of 1,2-dicarbonyl compounds strongly reduces the h.c.c. of manganese in the spin adducts formed during the photolysis [3]. According to their interpretation we assign the adducts formed with ACNQ, PQ and *o*-TCBQ in THF as having the structure



(A′)

where a carbonyl ligand is replaced by an ether molecule. However, a singly coordinated structure of the type (A) cannot be excluded as we expect for this adduct a value of a_{Mn} about one half of that observed in the species (B), in analogy to what we already obtained for the metal h.c.c. in the alkali metal ion pairs of quinones [7].

For the *o*-TCBQ system in THF, on continued irradiation, we obtained the adduct (D) which we found to be the final species of the photochemical reaction in benzene. Instead, in the latter solvent we observed firstly the paramagnetic intermediates of the type (B) and then of the types (C) and (D). The assignment of the spectra to structures (C) and (D) is based on the fact that in benzene the replacement of CO ligands could occur only by other *o*-TCBQ molecules. That the species (C) and (D) should involve more than one quinone molecule was supported by the observation that, when we reacted *o*-TCBQ and $Mn_2(CO)_{10}$ with the latter in excess, we obtained essentially the (B) adduct even after a comparatively prolonged irradiation.

It should be noted that the species (C) and (D) are not observed with other quinones [4] probably because their formation requires a strong π electron acceptor molecule which facilitates the replacement of a pair of CO ligands.

At variance with the behaviour of the quinone adducts, in the TCNQ and DDQ adducts the a_{Mn} value does not vary from the benzene solution to ethereal solvents and this was taken as an evidence that the same type of adduct is formed. Therefore a subsequent substitution of CO ligands by THF does not occur. Probably this is prevented by an inefficient π electron delocalization of the metal electrons into the TCNQ or DDQ ligands which renders insufficiently stable a system with less than five CO ligand molecules. The unequivalence of the nitrogen h.c.c.s ensures that the $\cdot Mn(CO)_5$ group is bound only to one nitrogen atom. A similar adduct was observed for TCNE [2].

We conclude by noting that in the DDQ molecule both carbonyl and nitrile groups are present and the bonding of $Mn(CO)_5$ to a nitrogen rather than to an oxygen atom is preferred.

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