MECHANISM OF THE PHOTOCHEMISTRY OF $Mn_2(CO)_{10}$ IN THE PRESENCE OF *para-* AND *ortho*-QUINONES

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Summary

The photochemical reaction of $Mn_2(CO)_{10}$ with *para-* and *ortho*-quinones has been studied by ESR spectroscopy in tetrahydrofuran, CH_3CN, and in 10^{-1} M pyridine in toluene. The *p*-quinone (2,6-di-t-butyl-1,4-benzoquinone) has been found to undergo an electron transfer with photogenerated $[Mn(CO)_{6-n}(S)_n]^{\cdot}$ radicals, $n = 1$–3, 19 e^- species producing $[Mn^I(CO)_{6-n}(S)_n^+] \cdot [$ *p*-semiquinone anion-radical$]$ ion-pairs, which undergo further photolysis leading to the $[Mn^I(CO)_{5-m}(S)_m($ *p*-semiquinone$)]$ radical-adducts; $m = 0$–2. These reactions take place alongside the photodisproportionation of $Mn_2(CO)_{10}$. It has been confirmed that *o*-quinones, on the other hand, act as good radical-traps, adding oxidatively to the photogenerated $Mn(CO)_5^{\cdot}$ radicals directly. The overall pattern of photochemical reactions of $Mn_2(CO)_{10}$ in the presence of coordinating reducible substrates is briefly discussed.

## Introduction

The photochemistry of $Mn_2(CO)_{10}$ and related complexes containing M–M single bonds is one of the most thoroughly studied topics in organometallic photochemistry [1–5]. It has been shown that $Mn_2(CO)_{10}$ undergoes two primary photoprocesses upon photoexcitation into its lowest energy absorption band, viz. Mn–Mn bond splitting leading to $Mn(CO)_5$ radicals and CO ligand dissociation producing $Mn_2(CO)_9$ species. The ample evidence for these two primary photoproducts and their chemical properties were recently reviewed [1–5]. The photochemically produced radical $Mn(CO)_5^{\cdot}$ is known to undergo dimerization, halogen abstraction from CCl_4, and substitution via an associative mechanism. The $Mn(CO)_5^{\cdot}$ radical and especially the 19 e^- species containing the coordinated solvent molecule, $Mn(CO)_5S^{\cdot}$, are strong reducing agents, which can also react via an electron-transfer mechanism [1,6] with various oxidizing agents and with $Mn_2(CO)_{10}$. The latter reaction plays a key role in the photodisproportionation of $Mn_2(CO)_{10}$, which dominates its photochemistry in donor solvents [1,4,5,7–9,35,36].

The $Mn(CO)_5^{\cdot}$ radicals can be also trapped by various organic substrates. Radical adducts of Mn^I with nitroxides are observed when $Mn_2(CO)_{10}$ is photolyzed in the presence of aromatic nitroso compounds in CH_2Cl_2, $CHCl_3$ or THF at low temperatures [7,10,11]. More stable radical adducts are formed with organic nitro-derivatives [12], and especially with 1,2-dicarbonyl compounds including *ortho*-quinones [13–21]. The reaction between photogenerated $Mn_2(CO)_{10}$ and *para*-quinone (2,6-di-t-butyl-1,4-benzoquinone) has been also monitored [20] by ESR spectroscopy in benzene solution with excitation by an N_2-laser. Formation of the free semiquinone anion-radical together with a radical adduct between $Mn(CO)_5$ and quinone containing Mn^I–C(3) bond has been postulated [20]. This reaction [20] and its product are quite unusual when compared with the outcome of related processes involving transition [23,24] and non-transition [33] metal species.

Two different mechanistic models have been invoked to explain these radical trapping reactions; (i) one-electron oxidative addition of organic species (aromatic nitroso compounds and organic nitro-derivatives [7,10–12]) to photogenerated $Mn(CO)_5$ radicals, and (ii) an electron transfer mechanism involving primary oxidation of $Mn_2(CO)_{10}$ by the substrate (e.g. tetracyanoethylene [22] or *para*-quinone [20]) leading to $Mn_2(CO)_{10}^{+}$, which subsequently decomposes to $Mn(CO)_5^{+}$ and $Mn(CO)_5^{\cdot}$. The latter species then traps another substrate molecule [15,20–22]. Both oxidative-addition [12–14,16–20] and electron-transfer [15,20,21] mechanisms have been applied to the photochemical reactions of $Mn_2(CO)_{10}$ with 1,2-dicarbonyl compounds and *ortho*-quinones, whereas the reaction with *p*-quinones has been interpreted in forms of the electron-transfer mechanism only [20].

Recently, reactions of *ortho*- and *para*-quinones with various transition metal complexes have been studied in this laboratory, and their mechanisms elucidated. Quinones were found to be useful probes of the chemical properties of transition metal complexes (including unstable photochemical intermediates) provided the reaction mechanism is studied in some detail [23–30]. In order to understand the reaction mechanism of radical-trapping and electron-transfer reactions of the products of the photolysis of $Mn_2(CO)_{10}$, and to reveal more information about the unusual reaction between $Mn_2(CO)_{10}$ and the 2,6-di-t-butyl derivative of *p*-quinone [20], we have carried out a systematic study of the mechanism of $Mn_2(CO)_{10}$ photolysis in the presence of various quinones *, namely *p*-DBQ and its *ortho*-isomer:

p–DBQ   o–DBQ

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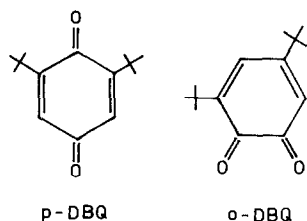
* The following abbreviations are used for the quinones: *o*-DBQ = 3,5-di-t-butyl-1,2-benzoquinone; PQ = 9,10-phenanthrenequinone; CQ = *o*-chloranil (3,4,5,6-tetra-chloro-1,2-benzoquinone), *p*-DBQ = 2,6-di-t-butyl-1,4-benzoquinone. One-electron reduced forms, i.e. semiquinone radical-anions are denoted SQ, e.g. DBSQ, CSQ, PSQ.

Experimental

$Mn_2(CO)_{10}$, PQ, and CQ were used as obtained from Fluka, whereas p-DBQ (Aldrich) was resublimed and o-DBQ (Aldrich) was recrystalized from heptane. Tetrahydrofuran (THF) (Fluka) was distilled from sodium/benzophenone under argon to give an oxygen- and moisture-free solvent, which was then handled under pure argon in a closed Schlenk-type apparatus. Toluene (Lachema, Brno) was repeatedly stirred with H_2SO_4 then distilled from P_2O_5 and finally from $LiAlH_4$. Pyridine (Merck) was distilled from KOH, whereas CH_3CN (Fluka) was used without any purification. All solvents except THF were degassed by bubbling argon through them. ESR and spectroscopic cells were filled in the dark under argon by use of syringes.

Samples were irradiated inside the ESR-cavity with light from a 200 W high-pressure mercury lamp HBO 200. Specific wavelengths were selected by appropriate glass filters (Carl-Zeiss, Jena).

ESR measurements were carried out at room temperature using a Varian E-4 instrument. 2,2-Diphenyl-1-picrylhydrazyl, DPPH, (Aldrich) was used as a standard ($g = 2.0037$) for the determination of g-values. Absorption spectra were measured on Carl-Zeiss Jena M 40 spectrophotometer.

Results and discussion

Reaction with 2,6-di-t-butyl-1,4-benzoquinone (p-DBQ)

Solutions of $Mn_2(CO)_{10}$ and p-DBQ in THF, CH_3CN, toluene or toluene/pyridine mixtures prepared in dark exhibit no ESR signals. The absorption spectrum of the mixture of 5×10^{-4} M $Mn_2(CO)_{10}$ with 5×10^{-3} M p-DBQ in THF or in toluene does not change with time when kept in dark. Moreover, these spectra are identical with the arithmetic sum of the spectra of separated $Mn_2(CO)_{10}$ and p-DBQ solutions. Thus, neither electron transfer reaction nor ground-state complex formation takes place between $Mn_2(CO)_{10}$ and p-DBQ without exposure to light.

When THF solutions containing $Mn_2(CO)_{10}$ and p-DBQ (usually both 10^{-2} M) are continuously irradiated with either polychromatic or monochromatic (365, 405, 436 nm) light, a broad poorly resolved ESR signal, A, is initially formed (Fig. 1). Its g-value is identical with that of the electrochemically-generated free p-DBSQ anion-radical, Tab. 1. However, its line-width is larger and the proton hyperfine splitting (hfs, not resolved) is much lower compared with those for free, unassociated p-DBSQ. This signal may be attributed to the ion-pair $[Mn^I(CO)_{6-n}(S)_n^+] \cdot [p\text{-}DBSQ]$ (S = solvent molecule, $n = 1$–3), the ion-pairing being responsible for the deformation of the ESR signal of the p-DBSQ anion-radical. (The a_H-value of p-DBSQ is known to be greatly sensitive to the solvent and counter-ion variations [31,32].) When the irradiation is interrupted, radical A decays within 1–2 min producing no ESR-active species.

During the irradiation, the amplitude of signal A quickly reaches a maximum and then progressively decreases (Fig. 2, 3). However, in the course of continuous irradiation another ESR signal, B, appears (Fig. 1). Its amplitude (Fig. 2, 3) starts to increase sharply after an induction period and then reaches a constant value (slowly decaying after longer irradiation). Signal B may be attributed to the Mn^I-(p-DBSQ) radical adduct. i.e. $[Mn^I(CO)_{5-m}(S)_m(p\text{-}DBSQ)]$, $m = 0$–2 species as it exhibits all

TABLE 1

ESR PARAMETERS FOR SEMIQUINONE ANION-RADICALS AND THEIR COMPLEXES WITH Mn^I (a-values in mT, estimated accuracy ± 0.005 mT, g-values determined with accuracy ± 0.0001)

Compound	THF			Toluene			Note
	g	a_{Mn}	a_H	g	a_{Mn}	a_H	
p-DBSQ	2.0051	–	0.20		–	–	^{a}
A	2.0051	–	–	2.0051^b	–	–	
B	2.0048	0.15	0.08	–	–	–	
p-DBSQ	–	–	–	2.0045	–	–	^{c}, ref. 20
Mn(CO)$_5$(p-DBSQ)	–	–	–	2.0032	0.71	0.34	^{c,d}, ref. 20
o-DBSQ	2.0051^a	–	0.32^a	2.0046^e	–	0.27^e	
Mn(CO)$_4$(O,O-DBSQ)	2.0037	0.69	0.34	2.0036	0.70	0.35	ref. 17
Mn(CO)$_3$(THF)(O,O-DBSQ)	2.0047	0.36	0.36	–	–	–	ref. 17
Mn(CO)$_3$(py)(O,O-DBSQ)	–	–	–	2.0041	0.61	0.32	^{h,f}
PSQ	2.0050^a	–	–	2.0045^e	–	–	
Mn(CO)$_4$(PSQ)	–	–	–	2.0038	0.55	–	^{c}
Mn(CO)$_3$(THF)(PSQ)	2.0044	0.27	–	–	–	–	
CSQ	2.0062^a	–	–	2.0063^e	–	–	
Mn(CO)$_4$(CSQ)	–	–	–	2.0036	0.88	–	ref. 17
Mn(CO)$_3$(THF)(CSQ)	2.0034	0.39	–	–	–	–	ref. 17

^{a} Electrochemically generated in the presence of 10^{-1} M Bu$_4$NPF$_6$. ^{b} 10^{-1} M pyridine added. ^{c} In benzene. ^{d} Six doublets [20]. ^{e} Corresponds to Na$^+ \cdot$ SQ ion pairs. ^{f} a_N 0.20 mT.
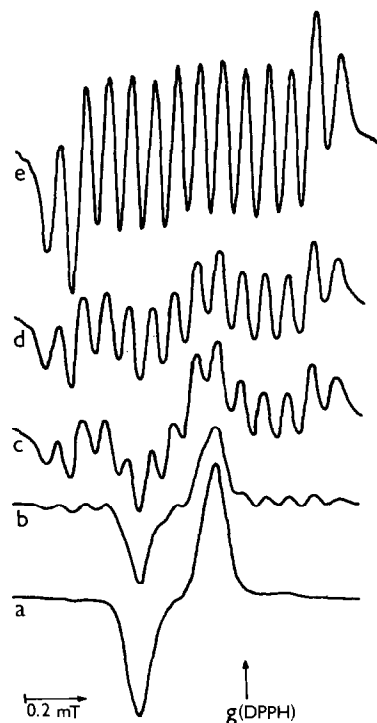
Fig. 1. ESR spectra of the radicals formed during continuous photolysis (366 nm) of a THF solution of $Mn_2(CO)_{10}$ and p-DBQ (both 10^{-2} M). a, radical A, recording started at the same time as irradiation; b, after 165 s of irradiation; c, after 350 s; d, after 840 s; e, radical B, measured in dark just after 10 s of polychromatic irradiation. (The signal amplitudes are not directly comparable due to different scales.)

the features characteristic of metal complexes containing a p-DBSQ radical-anionic ligand bonded to a diamagnetic central metal atom via its C(4)–oxygen donor atom [23,24,33]; the g-value of the B signal is slightly lower than that of free p-DBSQ and there is splitting by ^{55}Mn ($I = 5/2$) and the two symmetrically equivalent protons (bonded at C(3) and C(5) positions of the quinone) (Fig. 1). The manganese hfs is quite low (0.15 mT). Furthermore, the proton hfs (0.08 mT) is characteristically lowered compared with that of free p-DBSQ (0.20 mT). When the irradiation is interrupted after the generation of the B signal, its amplitude slowly (tens of minutes) decays without the formation of any other ESR-active species.

The formation of the two radicals A and B, described above, takes place qualitatively in the same way irrespective of the irradiation wavelength (polychromatic or 365, 405, or 436 nm monochromatic light) or of the ratio of reactant concentrations ($Mn_2(CO)_{10}/p$-DBQ) which was varied in the range 8/1–1/20. The partial light absorbance of $Mn_2(CO)_{10}$ in most of the monochromatic experiments was as high as 99.6%, showing that the observed photochemistry originates from the photoexcitation of $Mn_2(CO)_{10}$. The only difference between the irradiation at 365 nm and at 436 nm is that with the latter there is a much shorter induction period for the formation of radical B and a lower relative yield of radical A (compare Figs. 2 and 3). The existence of the induction period for the formation of radical B together with the observation that the formation of this radical ceases immediately when the
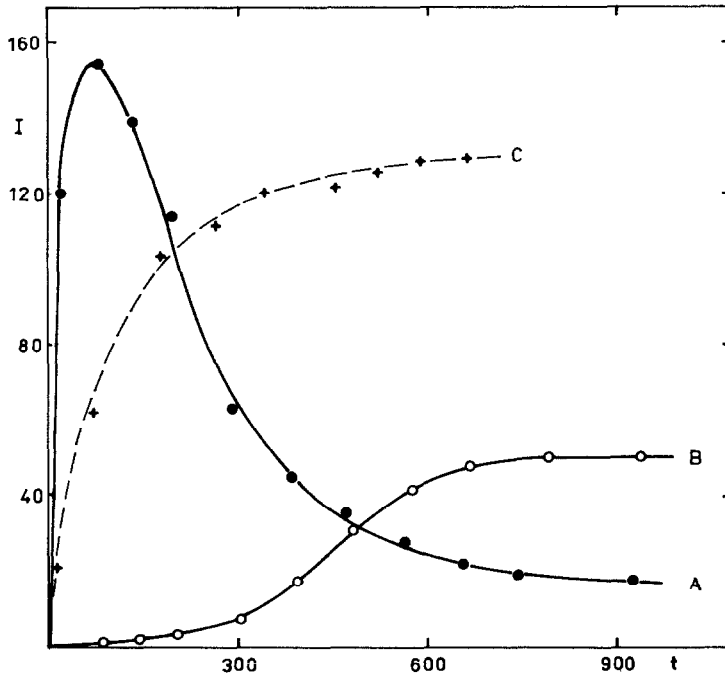
Fig. 2. The dependence of the ESR signal amplitudes on the time (s) of continuous 366 nm monochromatic irradiation. A (●): amplitude of signal A under high-intensity irradiation; B (○): amplitude of signal B under high-intensity irradiation; C (+): amplitude of signal A under low-intensity irradiation (multiplied by 5).
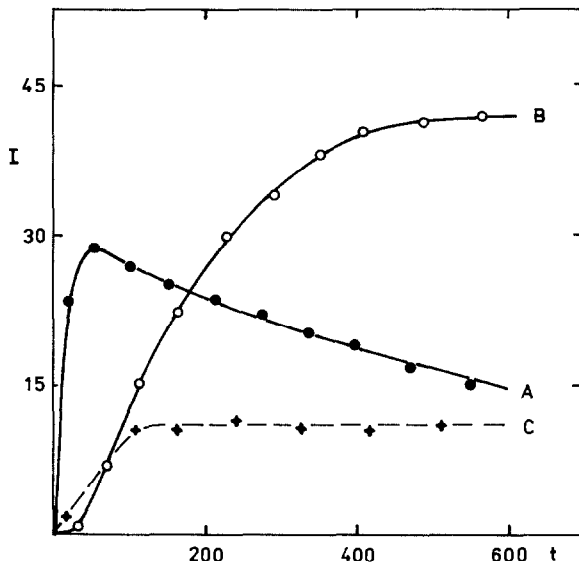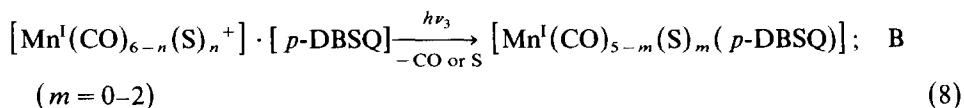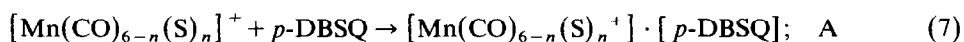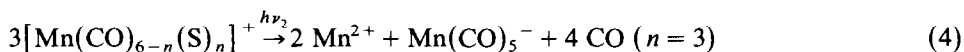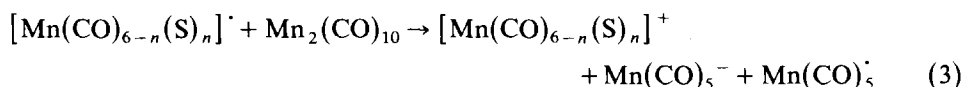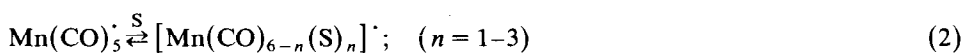

Fig. 3. The dependence of the ESR signal amplitudes on the time of continuous 436 nm monochromatic irradiation. See Fig. 2 for details.

irradiation is interrupted suggest that radical B is formed by a photolysis of some previously formed photochemical intermediate, most probably radical A. This conclusion is strongly supported by the influence of incident light intensity on the formation of both photoproducts: when the intensity was lowered to approximately 1/20 of the normal value by use of an iris only radical A was observed. The amplitude of the corresponding ESR signal increases slowly to reach an approximately constant value. The steep decrease found under intense irradiation was not observed (Figs. 2, 3). Radical B is not formed at all with low intensity irradiation. However, its formation starts soon after the incident light intensity is increased to the normal value. It is evident (Figs. 2, 3) that the formation of radical B requires intense irradation and is accompanied by a fall in the concentration of radical A, which is thus the most probable precursor of radical B. The shorter induction period at 436 nm than that at 365 nm shows that the extinction coefficient of the precursor of the formation of radical B (i.e. species A) is larger at the former wavelength.

The overall mechanism of the photochemical reaction of $Mn_2(CO)_{10}$ with p-DBQ may be represented by the following reaction sequence, which was substantiated by additional experiments described later.

$$Mn_2(CO)_{10} \overset{h\nu_1}{\rightleftarrows} 2\,Mn(CO)_5^{\cdot} \tag{1}$$

$$Mn(CO)_5^{\cdot} \overset{S}{\rightleftarrows} [Mn(CO)_{6-n}(S)_n]^{\cdot}; \quad (n = 1\text{–}3) \tag{2}$$

$$[Mn(CO)_{6-n}(S)_n]^{\cdot} + Mn_2(CO)_{10} \rightarrow [Mn(CO)_{6-n}(S)_n]^{+}$$
$$+ Mn(CO)_5^{-} + Mn(CO)_5^{\cdot} \tag{3}$$

$$3[Mn(CO)_{6-n}(S)_n]^{+} \overset{h\nu_2}{\rightarrow} 2\,Mn^{2+} + Mn(CO)_5^{-} + 4\,CO\ (n = 3) \tag{4}$$

$$[Mn^0(CO)_{6-n}(S)_n]^{\cdot} + p\text{-DBQ} \rightarrow [Mn^I(CO)_{6-n}(S)_n^{+}] \cdot [\,p\text{-DBSQ}]; \quad A \tag{5}$$

$$Mn(CO)_5^{-} + p\text{-DBQ} \rightarrow Mn(CO)_5^{\cdot} + p\text{-DBSQ} \tag{6}$$

$$[Mn(CO)_{6-n}(S)_n]^{+} + p\text{-DBSQ} \rightarrow [Mn(CO)_{6-n}(S)_n^{+}] \cdot [\,p\text{-DBSQ}]; \quad A \tag{7}$$

$$[Mn^I(CO)_{6-n}(S)_n^{+}] \cdot [\,p\text{-DBSQ}] \xrightarrow[-\,CO\ \text{or}\ S]{h\nu_3} [Mn^I(CO)_{5-m}(S)_m(\,p\text{-DBSQ})]; \quad B$$

$$(m = 0\text{–}2) \tag{8}$$

(Note that p-DBSQ is an anion-radical (p-DBQ$^-$). Thermal decompositions of radicals A and B are omitted.)

All the photochemistry observed is derived from the primary photodissociation of the Mn–Mn bond [1–6,34] to form $Mn(CO)_5^{\cdot}$ radicals (eq.1). It has been found that the formation of both radicals A and B is completely quenched by 2×10^{-2} M-1 M CCl_4, which is known [1,3,6,34] to quench the $M(CO)_5^{\cdot}$ radicals more effectively than it does the other primary photoproduct $Mn_2(CO)_9$. Concomitant quenching of both radicals A and B points to the conclusion that they are successive products formed in one reaction sequence and not in parallel reactions.

It is now generally accepted [1,4,5,9] that $Mn(CO)_5^{\cdot}$ radicals undergo rapid coordination of the solvent molecule in donor solvents to give $[Mn(CO)_{6-n}(S)_n]^{\cdot}$ radicals (probably $n = 3$ [9]). These 19 e$^-$ are strongly reducing species. They are known to react with $Mn_2(CO)_{10}$ via reaction 3, leading to the well-studied

[1,4,5,7–9,35,36] photodisproportionation of $Mn_2(CO)_{10}$ to $[Mn^I(CO)_{6-n}(S)_n]^+$ and $Mn(CO)_5{}^-$. The former species undergoes further disproportionation [1,4,5,8,9] in a second photochemical step (eq.4), ultimately producing Mn^{2+} ions. (The formation of Mn^{2+} involves an induction period analogous to that in the formation of the radical B [7].) Indeed, production of a weak broad signal corresponding to the formation of Mn^{2+} ions [7] was found to take place together with the signal for radical B. This shows that the formation of radicals A and B occurs alongside the photodisproportionation of $Mn_2(CO)_{10}$ via reactions 3 and 4.

The formation of radical A takes place via two routes: First, the $[Mn(CO)_{6-n}(S)_n]^{\cdot}$ 19 e^- species can reduce * p-DBQ to the anion-radical p-DBSQ which is bound to the oxidized $[Mn^I(CO)_{6-n}(S)_n]^+$ complex as a counter-ion (eq.5). The resulting $[Mn(CO)_{6-n}(S)_n^+] \cdot [p$-DBSQ] ion-pairs are responsible for the observed ESR signal A. The second route to the radical A involves the reduction of p-DBQ by $Mn(CO)_5{}^-$ (eq. 6) formed in the disproportionations (eqs. 3, 4). Their resulting p-DBSQ undergoes ion-pairing (eq. 7) with the second disproportionation product, i.e. $[Mn(CO)_{6-n}(S)_n]^+$ leading also to the formation of radical A. The existence of such a route was confirmed by a separate experiment, in which a THF solution of $Mn_2(CO)_{10}$ (10^{-2} M) was polychromatically irradiated in a quartz tube for 1–2 min and p-DBQ (10^{-2} M) was then added in the dark; a weak ESR signal of radical A appeared and then decayed without the formation of any other ESR-active species. Since the photolyzed solution of $Mn_2(CO)_{10}$ contains only the products of the reactions 3 and 4, formation of radical A by the sequence of reactions 6 and 7 was directly proved. Moreover, the electrochemically generated $Mn(CO)_5{}^-$ was found to reduce p-DBQ to p-DBSQ in THF in the presence of 10^{-1} M Bu_4NPF_6, but this reaction took place slowly (over some minutes). The reactions 6 and 7 must thus be only a minor source of radical A.

The involvement of the $[Mn(CO)_{6-n}(S)_n]^{\cdot}$ species in the formation of radical A (eq. 5) is supported also by the absence of any ESR-active species in irradiated solutions of $Mn_2(CO)_{10}$ and p-DBQ in noncoordinating solvents, such as CH_2Cl_2 or toluene.

Importantly, radical A is able to undergo further photolysis (eq. 8) leading to the dissociation of either CO or S (THF) ligands, which is followed by (or concerted with) the coordination of the counter-ion, i.e. p-DBSQ, producing radical B, formulated as $[Mn(CO)_{5-m}(S)_m(p$-DBSQ)], $m = 0–2$, a radical-adduct containing the p-DBSQ radical-anionic ligand coordinated to the Mn^I central atom through its C(4)–oxygen donor atom. The photochemical formation of radical B from the ion-pair A has been demonstrated by the time-dependence of the corresponding ESR signals under low- and high-intensity irradiation, as discussed above.

The reaction mechanism (eqs.1–8) also involves formation of $Mn(CO)_5^{\cdot}$ radicals, either by the disproportionation (eq.3) or by the oxidation of (eq.6) $Mn(CO)_5{}^-$ by p-DBQ. These $Mn(CO)_5^{\cdot}$ radicals again enter reaction 2 making the whole process cyclic.

The reaction sequence of reactions 1–8 may also be used to explain the photochemical behaviour of the $Mn_2(CO)_{10}/p$-DBQ system in other solvents. Thus

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* $[Mn(CO)_5(CH_3CN)]^{\cdot}$ complex is known [1,6] to reduce organic substrates, e.g. viologens, whose reduction potentials are comparable or even more negative than that of p-DBQ (-0.64 V vs. SCE).
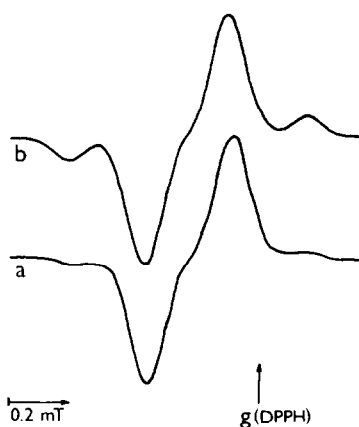
Fig. 4. ESR signals of radicals formed by photolysis of $Mn_2(CO)_{10}$ and p-DBQ (both 10^{-2} M) in 10^{-1} M pyridine/toluene. a, measured in dark after 3 s irradiation with 366 nm light; b, after irradiation with 436 nm light.
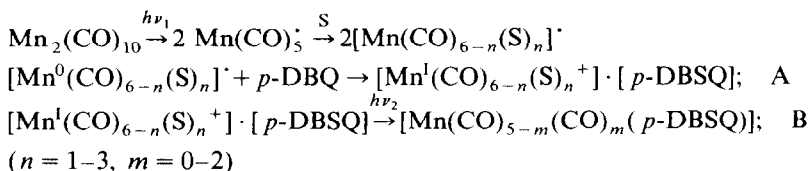
essentially the same results were obtained in CH_3CN as in THF, excluding any possible involvement of THF-derived radicals [7] in the photochemistry described above. Both radicals A and B are formed. Their formation is quenched by CCl_4. However, the relative yield of radical A is greater and that of radical B is lower in MeCN than in THF. Both these radicals decay in CH_3CN markedly faster than in THF. Moreover, reaction 4 does not take place in CH_3CN [9]. The disproportionation of Mn^I species to Mn^{2+} observed in THF is thus a parallel process, which is not necessarily involved in the formation of radicals A and B.

At the other hand, only the formation of radical A was observed in 10^{-1} M pyridine in toluene under polychromatic or monochromatic 366 or 436 nm irradiation at high or low intensity of the incident light (Fig. 4). The amplitude of the ESR signal corresponding to radical A is much higher in 10^{-1} pyridine/toluene than in THF or CH_3CN, and the signal decays only very slowly in dark. The formation of radical A is quenched by 10^{-1}–1 M CCl_4 (2×10^{-2} M CCl_4 does not quench its formation completely). When p-DBQ was added in dark to previously irradiated 10^{-2} M solution of $Mn_2(CO)_{10}$ in 10^{-1} M pyridine/toluene a quite intense A signal appears, in accord with the behaviour observed in THF. Under prolonged irradiation (especially at 436 nm) of the solution of $Mn_2(CO)_{10}$ and p-DBQ (both 10^{-2} M) in 10^{-1} M pyridine/toluene another weaker ESR signal, corresponding to free p-DBSQ unassociated with Mn^I-species, appears (Fig. 4). This signal is centered at exactly the same g-value as the signal A. The formation of free p-DBSQ was also observed after the addition of p-DBQ to the solution of $Mn_2(CO)_{10}$ in 10^{-1} M pyridine/toluene which had been previously irradiated by intense polychromatic irradiation for a long time.

These results may be explained as follows: The photodisproportionation of $Mn_2(CO)_{10}$ to Mn^{2+} and $Mn(CO)_5^-$ (eqs. 1–4) is known to be the prevailing process in pyridine or in pyridine (amine)/hydrocarbon solvents [7–9,35]. Alongside these reactions formation of radical A takes place via reactions 5 and 6–7. However, pyridine is a much stronger ligand than THF or CH_3CN, and so prevents formation of radical B via reaction 8. (Pyridine from the solvation shell competes

favourably with the p-DBSQ counter-ion). Moreover, the photodisproportionation of an Mn^I species to Mn^{2+} and $Mn(CO)_5^-$ (eq. 4) also competes with the formation of radical B more favourably in the presence of pyridine than in THF, and so radical B is not formed. However, the more pronounced photodisproportionation of Mn^I species liberates unassociated p-DBSQ anion-radicals, whose formation was observed after prolonged photolysis.

To sum up, the $Mn_2(CO)_{10}$ has been found to react photochemically with p-DBQ to give ultimately two radicals, A and B. The main reaction sequence involves two successive photochemical reactions, as in the following Scheme:

$$Mn_2(CO)_{10} \overset{h\nu_1}{\to} 2\ Mn(CO)_5^{\cdot} \overset{S}{\to} 2[Mn(CO)_{6-n}(S)_n]^{\cdot}$$

$$[Mn^0(CO)_{6-n}(S)_n]^{\cdot} + p\text{-DBQ} \to [Mn^I(CO)_{6-n}(S)_n^+]\cdot[p\text{-DBSQ}];\quad A$$

$$[Mn^I(CO)_{6-n}(S)_n^+]\cdot[p\text{-DBSQ}] \overset{h\nu_2}{\to} [Mn(CO)_{5-m}(CO)_m(p\text{-DBSQ})];\quad B$$

$(n = 1-3,\ m = 0-2)$

SCHEME 1

The last reaction may be blocked by the presence of strongly coordinating solvents, e.g. pyridine.

The photochemical reaction of $Mn_2(CO)_{10}$ and ortho-quinones

This reaction has already been studied. It has been found that $[Mn^I(CO)_5(O\text{-SQ})]$ is a primary product of the oxidative addition of o-quinones to photogenerated (eq. 1) $Mn(CO)_5^{\cdot}$ radicals in alkanes [18]:

$$Mn(CO)_5^{\cdot} + o\text{-Q} \to [Mn(CO)_5(O\text{-SQ})] \qquad (9) *$$

The final stable product containing chelated o-SQ ligand is formed by an intramolecular substitution [18]:

$$[Mn(CO)_5(O\text{-SQ})] \to [Mn(CO)_4(O,O\text{-SQ})] + CO \qquad (10)$$

In hydrocarbons, $[Mn(CO)_4(O,O\text{-SQ})]$ is the final reaction product, whereas in coordinating solvents or in the presence of various ligands a mixture of $[Mn(CO)_4(O,O\text{-SQ})]$ and (usually predominant) $[Mn(CO)_3(S)(O,O\text{-SQ})]$ complexes is formed [12–21].

Although direct trapping of $Mn(CO)_5^{\cdot}$ radicals by *ortho*-quinones is now generally regarded as responsible for the formation of o-semiquinone complexes of Mn^I [12–14,16–20], a mechanism involving primary electron-transfer between $Mn_2(CO)_{10}$ and o-quinones has been also postulated [15,20–22]. To throw light on this point, we undertook additional experiments, as follows.

No thermal redox reaction of $Mn_2(CO)_{10}$ with PQ, o-DBQ and even with strongly oxidizing o-CQ takes place in dark, as was shown by ESR-spectroscopy and by absorption spectroscopy in the UV-VIS region. Moreover, formation of ground state complexes between $Mn_2(CO)_{10}$ and o-quinones (studied for o-DBQ and PQ in THF and toluene) was also excluded spectroscopically.

The photolysis of toluene or THF solutions of $Mn_2(CO)_{10}$ with the corresponding o-quinone (both 10^{-2} M) was found to produce Mn^I complexes containing

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* O-SQ stands for monodentate o-semiquinone ligand coordinated to the metal central atom by one oxygen atom only. By analogy, the chelated, bidentate o-semiquinone ligand is denoted O,O-SQ.

chelated o-SQ (o-DBSQ, PSQ, CSQ) radical-anionic ligands. Their ESR spectra are identical with those in the literature (Tab. 1). Furthermore, a new radical complex [Mn(CO)$_3$(py)(O,O-DBSQ)] was found to be formed by the photolysis of Mn$_2$(CO)$_{10}$ with o-DBQ in 10^{-1} M pyridine/toluene. The amplitudes of the ESR signals corresponding to all these o-semiquinone complexes of Mn^I were much higher than those of radicals A and B formed in the reaction with p-DBQ under identical experimental conditions (initial reactant concentration, intensity and time of irradiation).

The concentration of the [Mn(CO)$_3$(THF)(O,O-DBSQ)] formed by the photolysis of Mn$_2$(CO)$_{10}$ with o-DBQ (both 10^{-2} M) increases linearly with the irradiation exposure time. No induction period and no effect of the incident light intensity was found, in full accord with direct trapping of photogenerated Mn(CO)$_5^.$ radicals by o-quinones via the oxidative addition mechanism (eq. 9 followed by rapid reaction 10).

During the photolysis of Mn$_2$(CO)$_{10}$ with o-quinones in toluene, THF or pyridine/toluene mixtures, no radicals other than [Mn(CO)$_{4-n}$(S)$_n$(O,O-SQ)], ($n = 0$, 1) complexes were observed. The primary electron-transfer between the Mn$_2$(CO)$_{10}$ dimer [20] or between [Mn(CO)$_{6-n}$(S)$_n$]$^.$ 19 e$^-$ species and o-quinones producing Mn^I complexes and free o-semiquinones is thus very improbable.

Mechanism of the photochemical reaction of Mn$_2$(CO)$_{10}$ with quinones

The photochemical reactions of Mn$_2$(CO)$_{10}$ with both *ortho-* and *para-*quinones discussed above reveals some more general features which may be summarized as follows:

1. There is no evidence for any (thermal or photochemical) electron-transfer reaction between undissociated Mn$_2$(CO)$_{10}$ and either *ortho-* or *para-*quinones * such as was assumed by other authors [15,20–22]. All the photochemistry was found to be derived from the Mn(CO)$_5^.$ primary photoproduct.

2. Different reaction paths have been found for the reaction of Mn$_2$(CO)$_{10}$ with *ortho-* and *para-*quinones. The *ortho-*isomers add oxidatively to the photogenerated Mn(CO)$_5^.$ radical, whereas the *para-*quinone reacts via an electron-transfer with [Mn(CO)$_{6-n}$(S)$_n$]$^.$ 19 e$^-$ species (eq. 5) and the radical-adduct [Mn^I(CO)$_{5-m}$-(S)$_m$(p-DBSQ)] is formed by a secondary photochemical reaction (eq. 8) and not by a direct radical-trapping. However, both *ortho-* and *para-*quinones are known to add oxidatively to various metal-centered radicals containing transition or main-group metal central atoms. The most relevant example is Co^{II}(CN)$_5^{3-}$, which is isostructural and isoelectronic with Mn(CO)$_5^.$. The Co^{II}(CN)$_5^{3-}$ radical-complex adds oxidatively to both o- and p-DBQ, producing radical-adducts of Co^{III} [23,24]. Two factors contribute to this difference between the reactivity of quinones with Mn(CO)$_5^.$ and Co(CN)$_5^{3-}$ complexes; (i) Whereas the Co(CN)$_5^{3-}$ can be oxidized only via oxidative additions [23,24], the Mn(CO)$_5^.$ radical can undergo oxidative additions [10–22] as well as simple electron transfer oxidations, especially after coordination of solvent molecules [1,4–6,9]. In contrast to the situation in the reaction involving Co(CN)$_5^{3-}$, competition between electron-transfer reactions (eqs.

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* Such electron-transfer could proceed photochemically only in some ground-state Mn$_2$(CO)$_{10}$·Q complexes since the lifetime of the excited Mn$_2$(CO)$_{10}$ is too short [1,37] for a bimolecular reaction. However, no evidence for such ground-state complexation has been found.

2, 3, 5, 6) and direct oxidative addition of p-DBQ to $Mn(CO)_5^-$ is thus possible in the $Mn(CO)_5^-/p$-DBQ system. (ii) Although the electron-transfer properties of *ortho*- and *para*-quinone isomers are analogous [26,38], the *o*-quinones, and especially the *o*-semiquinones, are much better ligands than the corresponding p-isomers, which form only very labile complexes when linked to the transition metal atom by the oxygen donor atom [23,24]. Moreover, the *o*-semiquinone bonding is greatly stabilized by chelate-ring formation [39]. As the oxidative addition involves electron-transfer along with M–O bond formation, the *o*-quinones react much more readily in this way than their p-isomers owing to much stronger M–*o*-semiquinone bonding in the product. When competition between electron transfer and oxidative addition is possible, as is the case of $Mn_2(CO)_{10}$ photochemistry, the electron transfer path will predominate in the case of p-quinones, whereas the oxidative additon (i.e. radical trapping) will predominate with the *o*-isomers.

3. As stated above, we did not observe any photochemical reactions in a toluene solution of $Mn_2(CO)_{10}$ and p-DBQ under irradiation with a 200 W mercury lamp. On the other hand formation of p-DBSQ and a radical-adduct containing p-DBSQ linked to the Mn^I central metal atom via an Mn–C(3) bond has been postulated to take place under irradiation with an intense (1 MW) nitrogen laser in benzene solutions [20]. On the basis of the results discussed above and the ability of $Mn(CO)_5^-$ to act as an electron transfer reducing agent even in noncoordinating solvents like CH_2Cl_2 [6], the formation of p-DBSQ (probably bound also in an ion-pair with some Mn^I cationic complex) observed in benzene [20] can be explained also by an electron-transfer from $Mn(CO)_5^-$ to p-DBQ, rather than by an electron-transfer from $Mn_2(CO)_{10}$ as suggested in ref. 20. The experiments reported in ref. 20 also do not prove that the radical-adduct formed in benzene is a primary product of the oxidative addition of p-DBQ to $Mn(CO)_5$.

4. In conclusion, the photochemical reactions of $Mn_2(CO)_{10}$ with substrates possessing both redox and coordinating properties can be explained in terms of a competition between the direct oxidative addition to the photogenerated $Mn(CO)_5^-$ radicals (i.e. radical-trapping) and an electron transfer reaction, which may be followed by some interaction between the redox products. The particular reaction path followed is determined by the redox properties of the substrates, by the bonding ability of their one-electron reduced forms, and by the nature of the solvent.

Acknowledgment

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