Studies of Thermal- and Photo-interconversions of Manganese Carbonyl Halide Species by Ultraviolet Spectroscopy

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$Mn(CO)_5X$ and $[Mn(CO)_4X]_2$ (X = Cl or Br) coexist in equilibrium in benzene solution, the position of equilibrium at a given temperature being determined by [CO]. Similarly, $Mn(CO)_3L_2X$ and $[Mn(CO)_3LX]_2$ [L = methyl methacrylate (mma) or acetonitrile (an)] are also easily interconverted. In mma (a weak donor) two substituted compounds are produced, $Mn(CO)_3(mma)_2X$ and $[Mn(CO)_3(mma)X]_2$, the former predominating in mma solution. Irradiation of $[Mn(CO)_3LX]_2$ (L = CO, an, or mma) with $\lambda = 435{\cdot}8$ nm produces manganese carbonyl, the yield of which is dependent upon the nature of L. $Mn(CO)_3L_2X$ also yields manganese carbonyl on photolysis, under conditions where the process $Mn(CO)_3L_2X \longrightarrow Mn(CO)_3LX + L$ is not inhibited by the presence of excess L. $Mn(CO)_3(mma)_2X$ is found to be an active photoinitiator of polymerization whereas $Mn(CO)_5X$ alone is not.

ALTHOUGH the kinetics of photoinitiation of free-radical polymerization by manganese carbonyl in the presence of halides has been investigated in some detail,[1-3] much less attention has been paid to the nature of the manganese-containing products and their possible intervention in the reaction at appreciable conversion. Kwok[4] showed that an almost quantitative yield of $Mn(CO)_5Br$ is obtained from the system $Mn_2(CO)_{10}$–HBr on irradiation ($\lambda = 435{\cdot}8$ nm) in cyclohexane solution. On the other hand, we found that irradiation of $Mn_2(CO)_{10}$–CCl_4 in benzene gives a yield of $Mn(CO)_5Cl$ considerably less than 100%. It appears that in solution $Mn(CO)_5Cl$ is unexpectedly labile, and readily forms other derivatives, such as the dimer $[Mn(CO)_4Cl]_2$, and complexes with weak donors which are present, including the methyl methacrylate monomer. These products show photochemical activity. An understanding of the chemistry of the $Mn_2(CO)_{10}$–CCl_4 system (except in the earliest stages of reaction) therefore requires a knowledge of interconversion processes involving the primary products.

This paper is mainly concerned with an investigation of the reactions of $Mn(CO)_5X$ (X = Cl or Br) and of the structure and reactions of the complexes formed with weak donors. (Although many instances of the formation of donor complexes by CO replacement by strong ligands have been reported,[5-7] we have not found any reference to related complexes with weak donors.) U.v. absorption spectroscopy has proved a most useful technique in this work; spectroscopic studies so far reported on systems related to those considered in this paper are relatively few in number, and appear to be confined to $Mn(CO)_5X$ and the dimeric species.[8,9] Spectral data for the complexes we have studied are collected in the Table.

EXPERIMENTAL

Materials.—Manganese carbonyl (Alfa Inorganics) was purified by sublimation at room temperature under a pressure of 10^{-4} Torr and stored in the dark. Manganese pentacarbonyl halides were synthesised and purified according to the method of Abel and Wilkinson.[6] $[Mn(CO)_4Br]_2$ Was prepared as described in the literature[5] and purified by vacuum sublimation. $[Mn(CO)_4Cl]_2$ Was prepared from manganese pentacarbonyl chloride by refluxing the latter in light petroleum (b.p. 40—60°) under nitrogen. The compound was purified by vacuum sublimation. $Mn(CO)_3$-$(MeCN)_2Br$ Was prepared and purified according to the method of Farona and Kraus.[10] $[Mn(CO)_3(MeCN)Br]_2$ Was synthesised from manganese pentacarbonyl bromide as described by Dunn and Edwards.[11] AnalaR carbon tetrachloride was used without further purification. *N*-Bromosuccinimide was recrystallized from water and stored in a

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[1] C. H. Bamford, P. A. Crowe, and R. P. Wayne, *Proc. Roy. Soc.*, 1965, **A284**, 455.

[2] C. H. Bamford, P. A. Crowe, J. Hobbs, and R. P. Wayne, *Proc. Roy. Soc.*, 1966, **A292**, 153.

[3] C. H. Bamford and J. Paprotny, *Polymer*, 1972.

[4] J. C. Kwok, Thesis, University of Liverpool, 1971.

[5] F. Zingales and V. Sartorelli, *Inorg. Chem.*, 1967, **6**, 1243.

[6] E. W. Abel and G. Wilkinson, *J. Chem. Soc.*, 1959, 1501.

[7] R. J. Angelici and F. Basolo, *J. Amer. Chem. Soc.*, 1962, **84**, 2495.

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[9] C. C. Addison, M. Kilner, and A. Wojcicki, *J. Chem. Soc.*, 1961, 4839.

[10] M. F. Farona and K. F. Kraus, *Inorg. Chem.*, 1970, **9**, 1700.

[11] G. Dunn and D. A. Edwards, *J. Organometallic Chem.*, 1971, **27**, 73.

vacuum desiccator. Benzene was dried by azeotropic distillation. Acetonitrile was dried over molecular sieve (type 4A) and then distilled *in vacuo*. Methyl methacrylate was rigorously purified as described by Bamford and Finch.[12] Nitrogen (British Oxygen Co.) and carbon monoxide (Matheson Co. Ltd.) were obtained from cylinders and used without further purification.

Spectroscopic Studies.—Absorption spectra were recorded with a Unicam SP 800 spectrophotometer with the aid of quartz cells with path lengths ranging from 0·1 to 10 cm. These cells were attached to Pyrex vessels by graded seals for the purpose of high vacuum studies.

Spectral data for manganese carbonyl halide complexes

Compound	Solvent	$\lambda_{max.} \pm 2$ nm	$10^3\ \varepsilon_{max.}$
$Mn_2(CO)_{10}$	C_6H_6	342	19·5
$Mn(CO)_5Cl$	C_6H_6	376	0·62
$Mn(CO)_5Br$	C_6H_6	381	0·42
	mma	380	0·42
$[Mn(CO)_4Cl]_2$	C_6H_6	416; *ca.* 340	1·66; 1·06
$[Mn(CO)_4Br]_2$	C_6H_6	426; *ca.* 340(sh)	1·4; 1·17
	mma	426; *ca.* 340(sh)	1·6
$Mn(CO)_3(mma)_2Cl$	mma	394	1·1
$Mn(CO)_3(mma)_2Br$	mma	396	*ca.* 9
$[Mn(CO)_3(mma)Br]_2$	mma	417; *ca.* 384(sh)	
$Mn(CO)_3(an)_2Br$	an	377	1·5
	C_6H_6 (2% an)	377	
$[Mn(CO)_3(an)Br]_2$	C_6H_6	420; *ca.* 370(sh)	1·8; 1·5
$Mn(CO)_3(an)_2Cl$	C_6H_6 (2% an)	376	*ca.* 1·2
*$Mn(CO)_3(etac)_2Cl$	C_6H_6–$MeCO_2Et$ (1 : 1)	391	
*$Mn(CO)_3(Et_2O)_2Cl$	Et_2O	400	

* Tentative formulae; etac = Ethyl acetate.

The extinction coefficients of acetonitrile complexes were estimated from optical density comparisons with compounds of known extinction coefficient (usually the manganese pentacarbonyl halide dimers).

Photochemical Studies.—Samples were irradiated under high vacuum with a parallel beam of light (λ = 435·8 nm) produced by an optical system similar to that described in an earlier publication.[1]

Carbon Monoxide Evolution.—The complex ($Mn(CO)_5X$ or $[Mn(CO)_4X]_2$) was dissolved in methyl methacrylate contained in a vessel fitted with a greaseless stopcock and the mixture degassed completely. Reaction was allowed to proceed in the dark at 25 °C; at suitable intervals the mixture was cooled to −196 °C and the carbon monoxide removed by a Toepler pump. Thaw–freeze cycles ensured complete removal of the gas. The reaction was continued until no further carbon monoxide was evolved.

RESULTS AND DISCUSSION

Thermal Interconversion of $Mn(CO)_5X$, $[Mn(CO)_4X]_2$, *and Related Species*.—(*a*) *Inert solvents*. The u.v. absorption spectrum of $Mn(CO)_5Cl$ in benzene solution is presented in Figure 1(*a*). This spectrum, which is consistent with data in the literature,[8] is shown only by freshly-prepared solutions. On allowing the solution to stand in air, or more rapidly on evacuation, a shoulder develops at *ca.* 416 nm [Figure 1(*b*)]; repeated degassing or flushing with nitrogen results in complete replacement of the original peak at 376 nm by one at 416 nm [Figure 1(*c*)]. The latter spectrum corresponds exactly with that of a solution of the dimer $[Mn(CO)_4Cl]_2$ in benzene. When the concentration of carbon monoxide in solution is kept low by a stream of nitrogen the transformation from $Mn(CO)_5Cl$ to $[Mn(CO)_4Cl]_2$ follows first-order kinetics, as is apparent from Figure 2; the first-order rate constant at 25 °C is $k_1 = 3{\cdot}7 \times 10^{-4}\ s^{-1}$.

The reaction may be completely reversed by addition of carbon monoxide. When a pressure of 1 atm CO is present the optical density at 416 nm decays in a first-order manner with a rate constant $k_{-1} = 1{\cdot}5 \times 10^{-3}\ s^{-1}$ at 25 °C.

Essentially similar results are obtained with $Mn(CO)_5Br$. As shown in Figure 2 the formation of $[Mn(CO)_4Br]_2$ occurs more slowly at 25 °C ($k_1 = 4{\cdot}6 \times 10^{-5}\ s^{-1}$); the reverse reaction is also slower ($k_{-1} = 7{\cdot}6 \times 10^{-4}\ s^{-1}$). The lower reactivities of the bromo-derivatives are consistent with the relatively slow ligand exchange processes observed with these compounds by Angelici and Basolo,[7] and by Zingales and Sartorelli.[5]

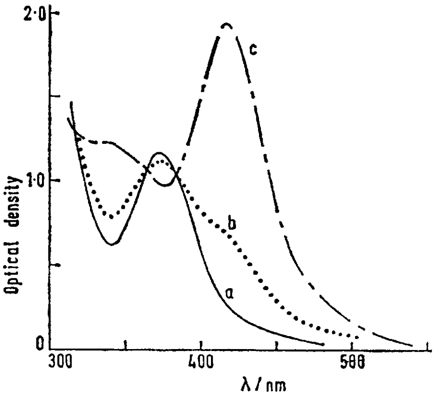

FIGURE 1 Absorption spectrum of $Mn(CO)_5Cl$ ($1{\cdot}93 \times 10^{-3}$ mol l^{-1}) in benzene; 5 min after preparation ——; after flushing with nitrogen for 15 min · · · ·; after flushing with nitrogen for 90 min

These results are in accordance with the reactions shown in equation (1). Comparison of the optical densities before and after reaction (utilizing the appropriate

$$Mn(CO)_5X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \tfrac{1}{2}[Mn(CO)_4X]_2 + CO \qquad (1)$$

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[12] C. H. Bamford and C. A. Finch, *Proc. Roy. Soc.*, 1962, **A268**, 553.

extinction coefficients) and the existence of the isosbestic points in Figure 1 indicate that these processes occur quantitatively. The values of k_1 we have obtained are reasonably close to the first-order constants for ligand exchange for $Mn(CO)_5Cl$ and $Mn(CO)_5Br$ at 25 °C which are derivable from the data of Angelici and Basolo.[7] These authors have shown that the rate-determining step is CO-scission and a similar conclusion seems applicable in the present case. The reaction mechanism is therefore that shown in equation (2).

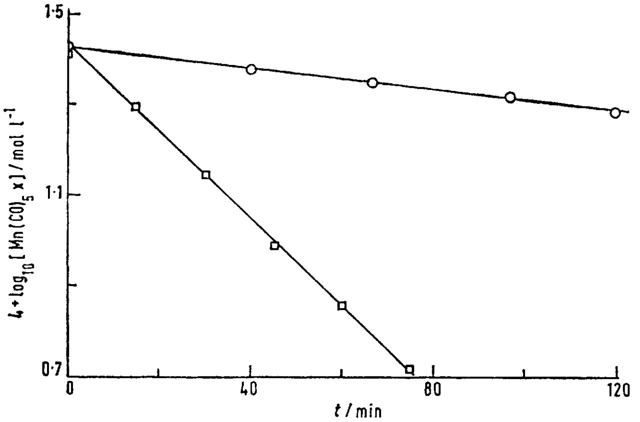


FIGURE 2 Dependence of $[Mn(CO)_5X]$ on reaction time t at 25 °C. □, X = Cl, ○, X = Br. Solvent-benzene; [CO] $\sim$ 0

$$\begin{aligned} Mn(CO)_5X &\xrightarrow{k_1} Mn(CO)_4X + CO \\ 2Mn(CO)_4X &\xrightarrow{\text{fast}} [Mn(CO)_4X]_2 \end{aligned} \qquad (2)$$

(*b*) *Donor solvents.* It is well-known that $Mn(CO)_5X$ and $[Mn(CO)_4X]_2$ form complexes with strong n-donors by ligand substitution. We now present evidence that complex formation also occurs with weaker donors such as methyl methacrylate, ethyl acetate, and ether. In view of the possible participation of monomer complexes in the initiation of polymerization of methyl methacrylate by the manganese derivatives we thought it desirable to investigate these compounds in some detail.

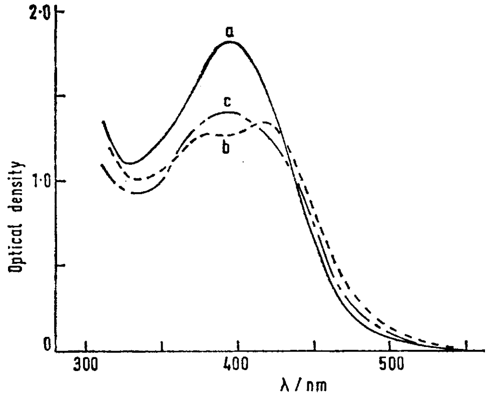
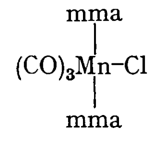


FIGURE 3 Absorption spectra of mma complexes produced from manganese carbonyl halides in mma solution; $[Mn(CO)_4Cl]_2$ (6×10^{-4} mol l^{-1}) in mma, recorded after 5 min ——; $[Mn(CO)_4Br]_2$ ($7{\cdot}5 \times 10^{-4}$ mol l^{-1}) in mma; recorded after 5 min - - - -; recorded after 25 min — — — —

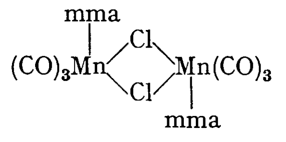
A solution of $[Mn(CO)_4Cl]_2$ in methyl methacrylate (mma) has the absorption spectrum shown in Figure 3(a); an identical spectrum may be obtained from a solution of $Mn(CO)_5Cl$ in the same solvent if free CO is removed by a stream of nitrogen. Measurements of the evolution of carbon monoxide show that at 25 °C two molecules of CO are liberated per molecule of $Mn(CO)_5Cl$ and $[Mn(CO)_4Cl]_2$ when dissolved in mma, suggesting that the complex responsible for the absorption spectrum in Figure 3(a) has a structure represented by (I) or (II), in which mma represents a methyl methacrylate ligand.



$$(CO)_3\overset{\text{mma}}{\underset{\text{mma}}{Mn}}\text{-}Cl$$

$Mn(CO)_3(mma)_2Cl$

(I)



$[Mn(CO)_3(mma)Cl]_2$

(II)

Similar spectroscopic studies with the corresponding bromides in mma revealed differences in behaviour. A solution of $Mn(CO)_5Br$ in mma initially exhibited a spectrum almost identical with that of a solution of the same compound in benzene; flushing with nitrogen, however, resulted in the formation of a mma complex as typified by an increase in the optical density and a bathochromic shift of the absorption maximum. Complex formation was, however, much slower than with $Mn(CO)_5Cl$ in mma. $[Mn(CO)_4Br]_2$ Showed more complicated behaviour than the corresponding chloride complex since the spectrum of its solution in mma changed with time. Five minutes after preparation of the solution, the spectrum exhibited a maximum at 417 nm and a shoulder at 384 nm [Figure 3(b)]. After 25 min the spectrum had broadened and had a peak at *ca.* 396 nm [Figure 3(c)]: no further change occurred on standing. Evidence that spectrum 3(b) did not arise from $[Mn(CO)_4Br]_2$ in mma solution was obtained by studying the reactions of this complex in mma saturated with carbon monoxide. It was anticipated that the latter would retard replacement of CO ligands by mma. Further, to minimize the conversion of $[Mn(CO)_4Br]_2$ to $Mn(CO)_5Br$ during solution in mma containing CO it was desirable to prepare the solution very rapidly; this was achieved by dissolving the complex in a small volume of benzene and adding the liquid to the mma saturated with carbon monoxide. The final mixture contained only 3% v/v of benzene, which would have a negligible effect on the absorption spectrum. The spectrum obtained initially corresponded closely with that of $[Mn(CO)_4Br]_2$ in benzene (Table). Conversion of $[Mn(CO)_4Br]_2$ to $Mn(CO)_5Br$ in mma under one atmosphere of CO proceeded with a half-life close to 5 min at 25 °C; this reaction is therefore approximately three times as fast in mma as in benzene. It is clear, therefore, that the absorption spectrum of $[Mn(CO)_4Br]_2$ under our conditions can only be observed if a technique ensuring rapid solution is adopted. These experiments show that the spectrum of Figure 3(b) corresponds to a complex containing mma.

A study of spectra of Figure 3(b) and 3(c) suggests that mma solutions of $[\mathrm{Mn(CO)_4Br}]_2$ contain, in general, two different mma complexes and we have endeavoured to clarify the situation by comparative spectroscopic studies on known acetonitrile (an) complexes with corresponding structures, *i.e.* $\mathrm{Mn(CO)_3(an)_2Br}$ and $[\mathrm{Mn(CO)_3(an)Br}]_2$. A few experiments have also been carried out with the chloride complexes.

Solutions of $\mathrm{Mn(CO)_3(an)_2Br}$ and $[\mathrm{Mn(CO)_3(an)Br}]_2$ in benzene show identical absorption spectra [Figure 4(a)]. Addition of acetonitrile (0·1% v/v) causes a spectral change which is effectively complete in 20 min [Figure 4(a)—(d)], the final spectrum corresponding closely to that of $\mathrm{Mn(CO)_3(an)_2Br}$ in acetonitrile (Table). These results imply that in benzene solution both complexes acquire the structure $[\mathrm{Mn(CO)_3(an)Br}]_2$ which in the presence of acetonitrile is transformed into $\mathrm{Mn(CO)_3(an)_2Br}$. Equilibrium (3) is therefore proposed.

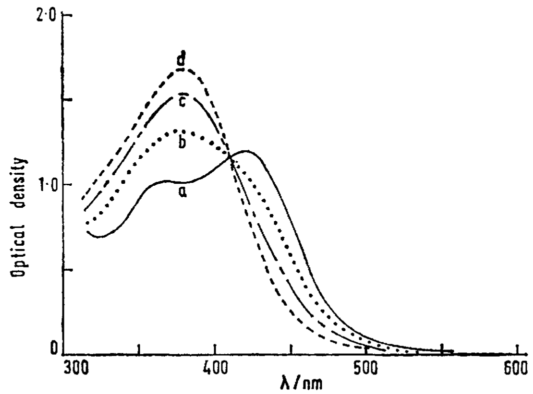
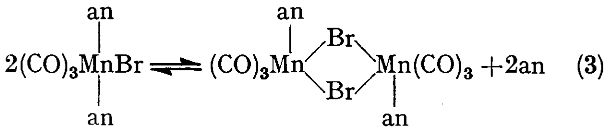


FIGURE 4 Absorption spectrum of $[\mathrm{Mn(CO)_3(an)Br}]_2$ ($5{\cdot}4 \times 10^{-5}$ mol $\mathrm{l^{-1}}$) in benzene. Effect of addition of acetonitrile, (0·1%, v/v): spectrum recorded after t min, $t = 3$ · · · ·; $t = 8$ ———; $t = 19$ - - - -



$$2(\mathrm{CO})_3\mathrm{Mn(an)_2Br} \rightleftharpoons (\mathrm{CO})_3(\mathrm{an})\mathrm{Mn}(\mu\text{-}\mathrm{Br})_2\mathrm{Mn(an)(CO)_3} + 2\mathrm{an} \qquad (3)$$

A similar reaction has been performed by Farona and Kraus [10] who dissolved $\mathrm{Mn_2(CO)_6(NC[CH_2]_3CN)Cl_2}$ (a bridged dinitrile complex) in acetonitrile and observed the formation of $\mathrm{Mn(CO)_3(an)_2Cl}$. We have also prepared solutions of $\mathrm{Mn(CO)_3(an)_2Cl}$ and $\mathrm{Mn(CO)_3(an)_2Br}$ in benzene by the addition of acetonitrile [2% (v/v)] to benzene solutions of $[\mathrm{Mn(CO)_4Cl}]_2$ and $[\mathrm{Mn(CO)_4Br}]_2$, respectively. The spectra obtained during these transformations did not show isosbestic points, indicating the intermediate formation of $[\mathrm{Mn(CO)_3(an)Cl}]_2$ and $[\mathrm{Mn(CO)_3(an)Br}]_2$. This first step is completely reversible since, when CO was passed through a solution of $[\mathrm{Mn(CO)_3(an)Br}]_2$ in benzene, the acetonitrile ligands were displaced with the consequent formation of $[\mathrm{Mn(CO)_4Br}]_2$. When $[\mathrm{Mn(CO)_3(an)Br}]_2$ is dissolved in mma the solution shows only the absorption spectrum of the mma complex [Figure 3(c)]. On passing carbon monoxide through the liquid, or through the final solution obtained from $[\mathrm{Mn(CO)_4Br}]_2$ in mma, ligand exchange occurs resulting in the formation of $\mathrm{Mn(CO)_5Br}$, the reaction being complete within 30 s. The spectrum after this period exhibited a slight shoulder at 426 nm which was not due to the mma complex, but which corresponded to the presence of $[\mathrm{Mn(CO)_4Br}]_2$, presumably produced by ligand exchange of CO with mma in $[\mathrm{Mn(CO)_3(mma)Br}]_2$. Since the conversion of $[\mathrm{Mn(CO)_4Br}]_2$ to $\mathrm{Mn(CO)_5Br}$ in mma is slow ($t_{\frac{1}{2}}$ *ca.* 5 min) relative to the rate of CO exchange with the mma complex it would appear that the above results are consistent with structure (I) as the main form of the complex in mma. The same conclusions were drawn from similar experiments performed upon solutions of the mma complexes of the chlorides.

Support for these views is obtained from comparison of the spectra of the mma solutions and those of solutions of acetonitrile complexes in benzene.

The spectrum in Figure 4(a) has similarities with that in Figure 3(b), suggesting that the first mma complex obtained upon solution of $[\mathrm{Mn(CO)_4Br}]_2$ in mma is $[\mathrm{Mn(CO)_3(mma)Br}]_2$. Furthermore, the spectra in Figures 3(a) and (c) show only one absorption maximum and are somewhat similar to the spectrum in Figure 4(d), suggesting that the mma complexes finally achieve structures $\mathrm{Mn(CO)_3(mma)_2Cl}$ and $\mathrm{Mn(CO)_3(mma)_2Br}$, respectively. That the final concentrations of $[\mathrm{Mn(CO)_3(mma)Cl}]_2$ or $[\mathrm{Mn(CO)_3(mma)Br}]_2$ in solutions of the mma complexes may not be negligible reflects the poor donor power of mma relative to acetonitrile. Also, no intermediate spectrum analogous to that of Figure 3(b) could be obtained upon solution of $[\mathrm{Mn(CO)_4Cl}]_2$ in mma (which is not surprising in view of the greater reactivity of the chloride compounds), and we presume that $\mathrm{Mn(CO)_3(mma)_2Cl}$ is produced by the mechanism holding for $\mathrm{Mn(CO)_3(mma)_2Br}$:

$$\left.\begin{array}{l}[\mathrm{Mn(CO)_4Br}]_2 + 2\mathrm{mma} \longrightarrow \\ \qquad\qquad [\mathrm{Mn(CO)_3(mma)Br}]_2 + 2\mathrm{CO} \\ [\mathrm{Mn(CO)_3(mma)Br}]_2 + 2\mathrm{mma} \rightleftharpoons \\ \qquad\qquad 2\mathrm{Mn(CO)_3(mma)_2Br}\end{array}\right\} \quad (4)$$

The Table shows that the absorption maxima for $\mathrm{Mn(CO)_3(mma)_2Cl}$ and $\mathrm{Mn(CO)_3(mma)_2Br}$ are situated at similar wavelengths. Although this may appear surprising in view of the data for $\mathrm{Mn(CO)_5Cl}$ and $\mathrm{Mn(CO)_5Br}$, the complexes $\mathrm{Mn(CO)_3(an)_2Cl}$ and $\mathrm{Mn(CO)_3(an)_2Br}$ also show maxima at effectively the same wavelength.

Photochemical Reactions.—(*a*) $\mathrm{Mn(CO)_5X}$ and $[\mathrm{Mn(CO)_4X}]_2$. When $[\mathrm{Mn(CO)_4Cl}]_2$ or $[\mathrm{Mn(CO)_4Br}]_2$ in benzene or cyclohexane solution is irradiated ($\lambda = 435{\cdot}8$ nm) in the absence of oxygen a rapid decomposition occurs. The spectral changes with $[\mathrm{Mn(CO)_4Br}]_2$ are illustrated in Figure 5, and represent a quantitative conversion into $Mn_2(CO)_{10}$ according to the equation:

$$2[Mn(CO)_4Br]_2 \longrightarrow Mn_2(CO)_{10} + 2MnBr_2 + 6CO \quad (5)$$

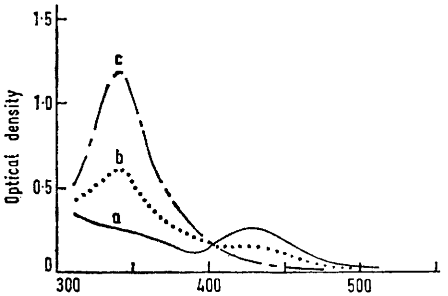
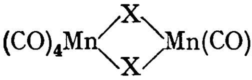


FIGURE 5 Effect of irradiation (λ = 435·8 nm) on the absorption spectrum of $[Mn(CO)_4Br]_2$ ($1{\cdot}9 \times 10^{-4}$ mol l^{-1}) in benzene. Formation of $Mn_2(CO)_{10}$ by irradiation for t min, $t = 0$ ——; $t = 4$ · · · ·; $t = 51$ — — — — —

Concentrated solutions of $[Mn(CO)_4X]_2$ became slightly cloudy on irradiation due to the separation of MnX_2; at the low concentration in the experiments of Figure 5 formation of $MnBr_2$ had no significant effect on the optical density. A plot of log $[Mn(CO)_4X]_2$ against time was linear at constant incident intensity. The chloro- and bromo-derivatives gave identical first-order constants. It seems likely that the primary photochemical reaction leading to (5) is that shown in (6). Manganese



$$(CO)_4Mn\langle X_2\rangle Mn(CO)_4 \xrightarrow{h\nu} (CO)_4MnX_2 + Mn(CO)_4$$
$$\longrightarrow 4CO + MnX_2 + Mn(CO)_4 \quad (6)$$

carbonyl is presumably formed from the fragment $Mn(CO)_4$ by reaction with carbon monoxide and dimerization, but the detailed reactions cannot be elucidated from data at present available.

In the presence of a halide such as carbon tetrachloride or *N*-bromosuccinimide (NBS) no manganese carbonyl can be detected, the final absorption being attributable to $Mn(CO)_5X$ unless steps are taken to remove the CO formed. Under these conditions $Mn(CO)_4$ is rapidly removed by reaction with the halide; a reaction of this kind has been postulated[2,3] as the radical-generating process in the photoinitiation of polymerization by manganese carbonyl in the presence of organic halides. If the photolysis is carried out in a vessel with small dead space the carbon monoxide formed in reaction (6) displaces the equilibrium in equation (1) to the left until only $Mn(CO)_5X$ is recognizable; continued irradiation is then without further effect. On the other hand, if the dead space is large, the concentration of $Mn(CO)_5X$ falls continuously on irradiation owing to the transformation of manganese derivatives into MnX_2 by reaction (6).

Experiments were carried out to ascertain whether irradiation of $Mn(CO)_5Cl$ or $Mn(CO)_5Br$ in benzene results in the production of manganese carbonyl. For this purpose CO at 1 atm was added to ensure the virtual absence of $[Mn(CO)_4X]_2$. On irradiation (λ = 435·8 nm) no $Mn_2(CO)_{10}$ was detected, and indeed no change of any kind was observable. This result automatically eliminates the possibility that $Mn_2(CO)_{10}$ might be formed *via* dimerization of $Mn(CO)_5$ produced by fission of the Mn–X bond (7) since the presence of CO should not affect the rate of decomposition of $Mn(CO)_5X$ according to (7).

$$Mn(CO)_5X \longrightarrow Mn(CO)_5 + X\cdot \quad (7)$$

In the absence of carbon monoxide manganese carbonyl is formed by irradiation of $Mn(CO)_5X$, and it must arise under these conditions through the operation of the equilibrium (1) and photolysis of the resulting dimer (6). The maximum rate of photolysis of $Mn(CO)_5X$ by this route should equal the rate of the forward reaction in (1). In an experiment with $Mn(CO)_5Br$ (λ = 435·8 nm) we observed a first-order decomposition with $k = 4{\cdot}3 \times 10^{-4}$ s^{-1}; since k_1 for the thermal reaction is almost an order of magnitude lower, the transformation of $Mn(CO)_5Br$ into the dimer must also proceed photochemically, probably by a route similar to reaction (2). Furthermore, irradiation of $Mn(CO)_5Br$ in mma produced manganese carbonyl at a rate comparable to that found in benzene solution. The final yield of $Mn_2(CO)_{10}$ was also similar. It was not possible to perform the equivalent reaction upon $Mn(CO)_5Cl$ in mma since in this case the formation of $Mn(CO)_3(mma)_2Cl$ prevents the preparation of a pure solution of $Mn(CO)_5Cl$ in mma. Irradiation of $Mn(CO)_5Br$ in mma did not produce any polymer.

Bamford *et al.*[13] have reported that the products of prolonged photolysis of $Mn_2(CO)_{10}$ in the presence of excess CBr_4 in ethyl acetate solution are capable of photo-initiating the polymerization of methyl methacrylate. This result is consistent with the reactions we have postulated, since the photochemical transformation of $Mn(CO)_5Br$ into the dimer, and decomposition of the latter according to reaction (6) would lead to $Mn(CO)_4$, which would produce initiating $\dot{C}Br_3$ radicals on reaction with CBr_4. Bamford *et al.*,[13] on the basis of experiments with $^{14}CBr_4$, suggested that some initiation by Br· atoms also occurs. This would not be expected; however, their results could be explained if a portion of the initiation arises from reaction between $Mn(CO)_4$ and unlabelled bromine-containing species (*e.g.* $BrCH_2CO_2Et$) produced during the first irradiation.

(*b*) *Acetonitrile and methyl methacrylate complexes.* A solution of $[Mn(CO)_3(an)Br]_2$ in benzene was irradiated (λ = 435·8 nm) *in vacuo*. A rapid decomposition occurred ($t_{\frac{1}{2}}$ *ca.* 1 min) and manganese carbonyl was produced with a yield of *ca.* 60% on the basis of the equation corresponding to (5). The other manganese-containing compounds so produced were not identified. We suggest that the increased rate of decomposition of this dimeric compound relative to $[Mn(CO)_4Br]_2$ in

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[13] C. H. Bamford, G. C. Eastmond, and F. J. T. Fildes, *Proc. Roy. Soc.*, 1972, **A326**, 453.

benzene ($t_{\frac{1}{2}}$ *ca.* 6 min) is due to the donor property of acetonitrile which produces weaker Mn–Br bonds.

Irradiation of $\mathrm{Mn(CO)_3(an)_2Br}$ in acetonitrile did not produce manganese carbonyl but gave rise to an alternative decomposition. The products from this reaction were not identified. However, when $\mathrm{Mn(CO)_3(an)_2Br}$, produced by the solution of either $\mathrm{Mn(CO)_3(an)_2Br}$ or $\mathrm{[Mn(CO)_3(an)Br]_2}$ in 0·1% (v/v) acetonitrile/benzene, was irradiated manganese carbonyl was produced in comparable yield to that obtained by irradiation of $\mathrm{[Mn(CO)_3(an)Br]_2}$ in $\mathrm{C_6H_6}$. These experiments recall the photolysis of $\mathrm{Mn(CO)_5Br}$ in the presence and absence of CO and suggest that upon irradiation $\mathrm{Mn(CO)_3(an)_2Br}$ decomposes to give $\mathrm{Mn(CO)_3(an)Br}$ which then dimerizes:

$$\left.\begin{array}{ll}\mathrm{Mn(CO)_3(an)_2Br} \overset{h\nu}{\rightleftharpoons} \mathrm{Mn(CO)_3(an)Br} + \mathrm{an} & \text{(a)}\\ \mathrm{2Mn(CO)_3(an)Br} \longrightarrow \mathrm{[Mn(CO)_3(an)Br]_2} & \text{(b)}\end{array}\right\} \quad (8)$$

In bulk acetonitrile the formation of $\mathrm{[Mn(CO)_3(an)Br]_2}$ is rigorously prevented whereas in 0·1% acetonitrile–benzene the concentration is sufficiently high for photolysis to occur.

Irradiation of solutions of $\mathrm{Mn(CO)_3(mma)_2X}$ ($\mathrm{X = Cl}$ or Br) in mma produced manganese carbonyl in low yield (<20%), the yield increasing with the initial concentration of complex. The formation of any manganese carbonyl is, however, significant since it again reflects the weak donor power of mma relative to acetonitrile. The photochemical production of $\mathrm{Mn(CO)_3(mma)X}$ and subsequent dimerization to $\mathrm{[Mn(CO)_3(mma)X]_2}$ (almost certainly the source of manganese carbonyl) are less subject to inhibition than the analogous reactions in acetonitrile.

Significantly, photolysis of the mma complexes also resulted in the initiation of polymerization, which is particularly interesting since no organic halide was present. There are many examples [1,2,14] of the initiating activity of transition metal carbonyl compounds in the presence of an organic halide (*e.g.* $\mathrm{CCl_4}$,NBS). We suggest that initiation in the present system must originate from the halide atom and we tentatively propose that reactions of the following type are involved.

$$\left.\begin{array}{ll}\mathrm{Mn(CO)_3(mma)_2X} \overset{h\nu}{\rightleftharpoons} & \\ \qquad \mathrm{Mn(CO)_3(mma)X} + \mathrm{mma} & \text{(a)}\\ \mathrm{Mn(CO)_3(mma)X} \longrightarrow \mathrm{Mn(CO)_3} + \mathrm{Xmma}\cdot & \text{(b)}\\ \mathrm{2Mn(CO)_3(mma)X} \longrightarrow \mathrm{[Mn(CO)_3(mma)X]_2} & \text{(c)}\\ \mathrm{[Mn(CO)_3(mma)X]_2} \xrightarrow{h\nu} & \\ \qquad \mathrm{MnX_2} + 3\mathrm{CO} + \mathrm{mma} + \mathrm{Mn(CO)_3(mma)} & \text{(d)}\end{array}\right\} \quad (9)$$

Reactions (9a,c,d) are analogous to (8a,b) and (6), respectively; the radical Xmma· formed in (9b) is responsible for initiation. The fates of the co-ordinatively unsaturated fragments arising in (9b,d) are not clear, but some reaction with carbon monoxide [liberated in (9d)] and subsequent recombination to form $\mathrm{Mn_2(CO)_{10}}$ must occur. The competition between the first- and second-order processes (9b,c) could account for the observed dependence of the yield of $\mathrm{Mn_2(CO)_{10}}$ on the initial concentration of $\mathrm{Mn(CO)_3(mma)_2X}$, since only (9c) leads to CO which is necessary for formation of $\mathrm{Mn_2(CO)_{10}}$.

The literature provides other examples of photoinitiation of polymerization by methyl methacrylate complexes. Mao and Eldred [15] suggested that the initiating species in the polymerization of mma photosensitized by $\mathrm{PPh_3}$ is an excited state of the complex mma←$\mathrm{PPh_3}$. More recently, Allen and co-workers [16] studied the photopolymerization of mma in the presence of $\mathrm{AlEt_3}$, and proposed on the basis of kinetic studies that the radical-generating species is a complex of the excited and ground states of mma→$\mathrm{AlEt_3}$.

(*c*) *Manganese carbonyl.* The results we have described are pertinent to the processes occurring during the photoinitiation of polymerization by $\mathrm{Mn_2(CO)_{10}}$–halide systems.[1-4] We have confirmed the formation of $\mathrm{Mn(CO)_5Cl}$ and $\mathrm{Mn(CO)_5Br}$ on irradiation ($\lambda = 435{\cdot}8$ nm) of solutions of $\mathrm{Mn_2(CO)_{10}}$ in benzene containing $\mathrm{CCl_4}$ and NBS respectively. If we accept the primary photolytic act and radical-generating reaction postulated in earlier publications [1-4] [(10a,b) respectively] it follows that the manganese pentacarbonyl halides must arise by interaction of $\mathrm{Mn(CO)_4X}$ with CO derived from $\mathrm{Mn(CO)_6}$. In earlier papers [2,3] we have suggested that $\mathrm{Mn(CO)_6}$ fragments form $\mathrm{Mn_2(CO)_{10}}$ and liberate CO according to reaction (11). An alternative process is provided by reaction (10c) followed by rapid recombination of $\mathrm{Mn(CO)_5}$ species, reaction (10d).

$$\left.\begin{array}{rl}\mathrm{Mn_2(CO)_{10}} \xrightarrow{h\nu} & \\ \mathrm{Mn(CO)_4} + \mathrm{Mn(CO)_6} & \text{(a)}\\ \mathrm{Mn(CO)_4} + \mathrm{RX} \longrightarrow \mathrm{Mn(CO)_4X} + \mathrm{R}\cdot & \text{(b)}\\ \mathrm{Mn(CO)_4X} + \mathrm{Mn(CO)_6} \longrightarrow & \\ \mathrm{Mn(CO)_5X} + \mathrm{Mn(CO)_5} & \text{(c)}\\ \mathrm{2Mn(CO)_5} \longrightarrow \mathrm{Mn_2(CO)_{10}} & \text{(d)}\end{array}\right\} \quad (10)$$

$$\mathrm{2Mn(CO)_6} \longrightarrow \mathrm{Mn_2(CO)_{10}} + 2\mathrm{CO} \quad (11)$$

In both cases the overall reaction is represented by

$$\tfrac{1}{2}\mathrm{Mn_2(CO)_{10}} + \mathrm{RX} \xrightarrow{h\nu} \mathrm{Mn(CO)_5X} + \mathrm{R}\cdot \quad (12)$$

which agrees with the observations that the quantum yield of radical formation is close to one,[1] and that each $\mathrm{Mn_2(CO)_{10}}$ decomposed yields two radicals (in the early stages of reaction).[4]

Assessed on the basis of reaction (12), the yield of $\mathrm{Mn(CO)_5X}$ is apparently not quantitative, although with NBS as halide it probably exceeds 93%. With $\mathrm{CCl_4}$ the yield of $\mathrm{Mn(CO)_5Cl}$ was only 60%. (The low yields

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[14] W. Strohmeier and P. Hartman, *Z. Naturforsch*, 1964, **19B**, 882.

[15] T. J. Mao and R. J. Eldred, *J. Polymer Sci. A*, 1967, **5**, 1741.

[16] P. E. M. Allen, B. O. Bateup, and B. A. Casey, *European Polymer J.*, 1972, **8**, 329.

do not reflect incomplete reaction of $Mn_2(CO)_{10}$, since at the end of photolysis the absorption spectra confirmed the absence of this compound.) We therefore believe that under our conditions secondary photolysis of $Mn(CO)_5X$ occurs, according to reactions (2) and (6). Thus, at high light intensities and high conversions, the radical-generating species $Mn(CO)_4$ may be produced not only by reaction (10a), but also by photoreactions involving $Mn(CO)_5X$.

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