

PHOTOINITIATION OF FREE-RADICAL POLYMERIZATION BY TRANSITION METAL DERIVATIVES

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ABSTRACT

Two types of photoinitiator are considered: (1) transition metal complexes (mainly carbonyls), (2) chelates of transition metals. In systems of type (1) the metal is in a low oxidation state and an organic halide is generally, but not always, present; on the other hand, in (2) the metal is initially in a high oxidation state. Comparison between photo- and thermal-initiation is made for each type.

Carbonyls of Group VIA metals undergo scission of CO on photolysis; the resulting species coordinates with monomer (or solvent) to form a complex which reacts with the halide (e.g. CCl_4) to generate initiating free radicals (e.g. $\dot{\text{C}}\text{Cl}_3$). Arguments are presented in favour of unsymmetrical photolysis of Group VIIA carbonyls [$\text{Mn}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_{10}$].

It is concluded that photoinitiation of free-radical polymerization by transition metal carbonyls may proceed by at least three routes: (i) electron-transfer to organic halide with rupture of a C—Cl or C—Br bond, (ii) reaction with a strongly electron attracting monomer such as C_2F_4 without rupture of C—F to form an initiating radical, (iii) hydrogen atom-transfer from monomer (or solvent) to a photoexcited metal carbonyl species.

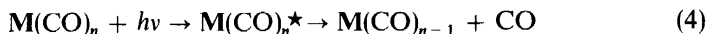
A study of photoinitiation by Mn^{III} acetylacetonate $\text{Mn}(\text{acac})_3$ and Mn^{III} 1,1,1-trifluoroacetylacetonate $\text{Mn}(\text{facac})_3$ shows that the monomer selectivity encountered in thermal initiation is absent. The quantum yield for initiation is low (10^{-2} to 10^{-3}) in both systems. With $\text{Mn}(\text{acac})_3$ the initiating process is scission of a ligand as a radical acac^\cdot , with formation of a Mn^{II} chelate; this reaction is not subject to significant solvent effects. On the other hand, photoinitiation by $\text{Mn}(\text{facac})_3$ shows strong dependence on the solvent and the data are interpreted in terms of exciplex formation between excited chelate and monomer (methyl methacrylate) or solvent (ethyl acetate). No exciplex is formed with benzene as diluent. A brief discussion of the natures of the photoexcited state and the state leading to decomposition is included.

We shall be concerned in this lecture with initiation of free-radical polymerization by systems of two types: (1) transition metal complexes with ligands such as carbon monoxide, aromatic isonitriles, triphenyl phosphite, generally, but not invariably, in the presence of organic halides and (2) chelates of transition metals. Systems of type (1) contain the metal in a low, often the zeroth, oxidation state, while in those of type (2) the metal is in a high oxidation state. It will later become apparent that the first group may be further subdivided depending on the precise mechanism of radical formation.

The simple kinetic schemes we have described are capable of accounting for most of the experimental data on systems of type (1). To summarize, under normal conditions the organometallic derivatives do not enter into direct reaction with the halide components of the initiating system: they are first converted into more reactive species by S_N1 or S_N2 processes.

Photoinitiation

Carbonyls of Group VIA—Ultra-violet irradiation ($\lambda < 350$ nm) of simple metal carbonyls results in scission of carbon monoxide and formation of a coordinatively unsaturated species:



In (4) **M** represents the metal atom. A summary of the experimental evidence with the relevant theoretical background for this type of primary photochemical process has been given in a review by Koerner von Gustorf and Grevels³. The product $\text{M}(\text{CO})_{n-1}$ may combine with carbon monoxide to regenerate the original carbonyl, or it may react by addition of an *n*- or π -donor **S** (e.g. the monomer) according to (5).

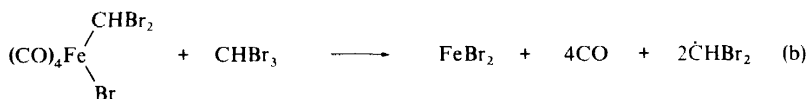
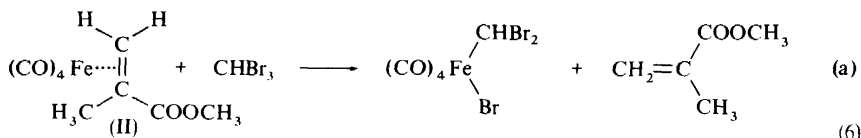


More complex reactions are also possible, for example, with other metal carbonyls in the system, or with certain molecules of type **X—Y** which may add with splitting of the **X—Y** bond.

Reactions (4) and (5) clearly constitute an S_N1 mechanism for ligand replacement. Their occurrence with Group VIA carbonyls and several types of *n*-donor has been demonstrated by Strohmeier and Dobson and their colleagues⁴⁻⁷. Many examples are known³ of photochemical substitution in transition metal carbonyls by *n*- and π -donors, occurring by processes essentially similar to (4) and (5). Ligand exchange by an S_N2 route is also possible with more complex carbonyls; here the photoexcited carbonyl reacts directly with the ligand before dissociation³. We shall not consider these reactions further here.

The species $\text{S} \cdots \text{M}(\text{CO})_{n-1}$ arising from (4), (5) are the same as the complexes, previously designated as (I), which are formed by the thermal reactions discussed earlier. They would therefore be expected to react with suitable halides in a manner represented by (3), with generation of free radicals. Thus mixtures of simple carbonyls and halides should behave as photoinitiators of free-radical polymerization. Many such systems have been found to function in this way, although the amount of mechanistic information deducible from the experimental results is unfortunately small. Complexes formed by irradiation of $\text{Fe}(\text{CO})_5$ in the presence of several olefinic monomers (**M**), including methyl methacrylate, vinyl chloride, styrene, propylene vinyl ethyl ether, and vinyl acetate have been studied by Koerner von Gustorf and colleagues^{8,9} and shown to have the structure $\text{MFe}(\text{CO})_4$, in which the iron atom is coordinated to the double bond [e.g. (II), equation (6)]. Similar adducts also arise from thermal reactions⁸. Further, it has been demonstrated⁸ that irradiation of the carbonyl in the presence of an organic halide leads to photoinitiated polymerization in suitable systems. Initiation

also occurs when the halide is added to the complex $MFe(CO)_4$ in the dark. It has been suggested³ that the reactions shown in (6) for $M =$ methyl methacrylate may be a possible source of free radicals.



Reaction (6a) involves splitting of the halide molecule and addition to the metal atom.

Strohmeier and Hartmann¹⁰ have reported photosensitization of the polymerization of ethyl acrylate by a number of metal carbonyls and related derivatives in the presence of carbon tetrachloride, and Strohmeier and Grübel¹¹ made similar observations on vinyl chloride. These authors did not suggest any detailed reaction mechanisms, but it seems most probable that reactions (4), (3) are responsible for photoinitiation.

When molybdenum carbonyl dissolved in ethyl acetate is irradiated a yellow solution containing $(\text{EtOAc})\text{Mo}(\text{CO})_5$ is formed, according to equations (4), (5) ($M = \text{Mo}$, $S = \text{EtOAc}$, $n = 6$)⁵⁻⁷. We have shown¹² that, when a solution of carbon tetrabromide in methyl methacrylate is added to this liquid, polymerization occurs in the dark at 25°C. The thermal rate of polymerization initiated by $\text{Mo}(\text{CO})_6/\text{CBr}_4$ (without irradiation) under these conditions is negligible in comparison. Clearly a reaction analogous to (3) leads to free-radical generation and initiation under these conditions. However, oxidation of molybdenum proceeds beyond the Mo^{I} stage, since during reaction the development of a characteristic electron-spin-resonance spectrum, attributable to a Mo^{V} species, may be observed^{12, 13}. Oxidation to this level also occurs during the thermal reaction at 80°C¹³. These experiments demonstrate that photochemical activation of the carbonyl enables a convenient separation to be made of the ligand-exchange and oxidation steps occurring in the thermal reaction, so that a more detailed quantitative examination of the initiation process becomes possible, somewhat analogous to the investigations on systems containing $\text{Ni}\{\text{P}(\text{O}Ph_3)\}_4$ made by Bamford and Hughes^{14, 15}.

Carbonyls of Group VIIA—Probably most attention has been paid to the Group VIIA carbonyls¹⁶⁻¹⁹, particularly manganese carbonyl. The absorption spectrum of manganese carbonyl in methyl methacrylate solution is shown in Figure 1; the same spectrum is obtained from benzene solutions. Photoinitiation occurs with high efficiency up to the long wave limit of absorption—460 nm, approximately. This carbonyl is therefore a very convenient photosensitizer, since it can be used with visible light. Most of our work has been carried out with light of $\lambda = 435.8$ nm, at which wavelength the extinction coefficient¹⁶ is $254 \text{ mol}^{-1} \text{ l cm}^{-1}$.

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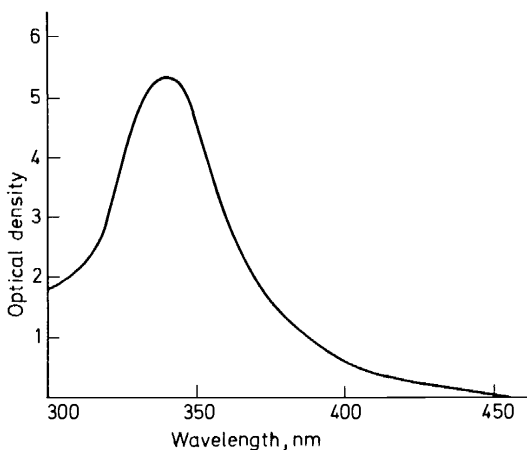
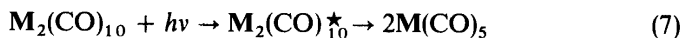


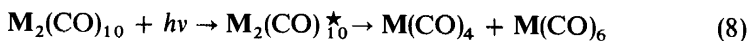
Figure 1. Ultra-violet absorption spectrum of manganese carbonyl in methyl methacrylate solution; path length 1 cm. $[\text{Mn}_2(\text{CO})_{10}] = 2.57 \times 10^{-4} \text{ mol l}^{-1}$.

The polymerization of methyl methacrylate photosensitized by $\text{Mn}_2(\text{CO})_{10}/\text{CCl}_4$ was first studied by Bamford, Crowe and Wayne¹⁶. At constant absorbed intensity, the rate of polymerization was found to depend on $[\text{CCl}_4]$ in the manner already described for thermal initiation. However, the sharpness of the dependence varies inversely with the absorbed intensity—the higher the intensity, the greater the value of $[\text{CCl}_4]$ required to achieve a given fraction of the limiting rate (see Figure 2). This observation suggests destruction of active intermediates by a process which is second-order in their concentration.

The quantum yield for photoinitiation at effectively limiting $[\text{CCl}_4]$ was shown to be close to unity¹⁶. Subsequently this result has been obtained with many other monomers (in fact, with all those studied)^{20, 21}. $\text{Re}_2(\text{CO})_{10}/\text{CCl}_4$ has only been examined with methyl methacrylate¹⁷; in this case also a similar quantum yield is found for short reaction times ($\lambda = 365 \text{ nm}$). (The reason for the restriction will become apparent later.) In all these systems, therefore, each quantum absorbed leads to one initiating radical. If the primary dissociation were the symmetrical fission



($\text{M} = \text{Mn}$ or Re) some component reaction (or combination of reactions) must be 50 per cent efficient to account for the observed quantum yield. Bamford, Crowe, Hobbs and Wayne¹⁷ reported that no carbon monoxide is evolved during irradiation of $\text{Mn}_2(\text{CO})_{10}$ in the absence of halide; they therefore suggested that the primary unsymmetrical fission (8) provides the most acceptable way of accounting for the quantum yield data.



It was supposed that only one of the dissociation products $\{\text{M}(\text{CO})_4\}$

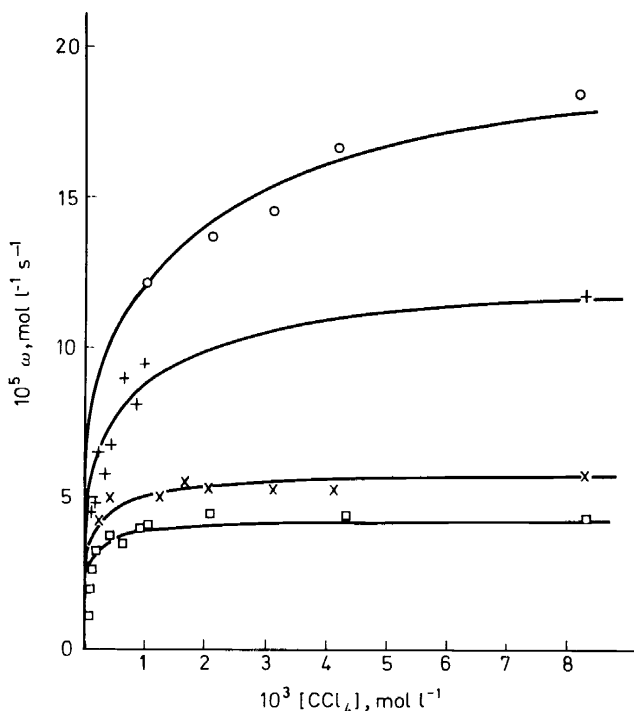
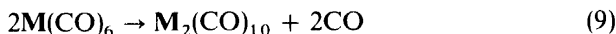


Figure 2. Rate of photosensitized ($\lambda = 435.8$ nm) polymerization of methyl methacrylate at 25°C as a function of carbon tetrachloride concentration. Values of $10^4[\text{Mn}_2(\text{CO})_{10}]/\text{mol l}^{-1}$: \circ 2.57, $+$ 2.57, \times 0.514, \square 2.57. Values of $10^8 I_{\text{abs}}/\text{einstein l}^{-1} \text{ s}^{-1}$: \circ 18.1, $+$ 6.04, \times 1.27, \square 0.664. Experimental data from ref. 16. Curves calculated from equation (11), present paper, $k_1 = 1$, $\alpha = 2.5 \times 10^{-5} \text{ s}^{-1}$.

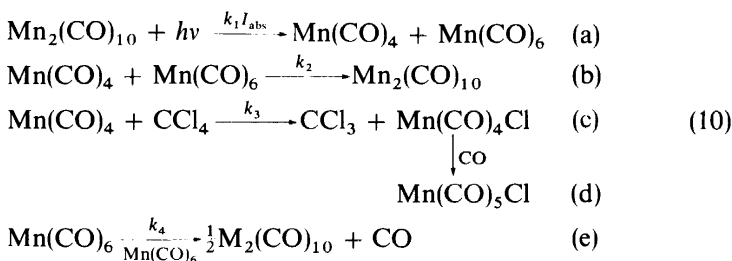
initiates polymerization by reaction with halide. This proposal was supported by observations on rhenium carbonyl which will be described below. According to the more recent findings of Kwok¹⁹, each molecule of $\text{Mn}_2(\text{CO})_{10}$ consumed generates two radicals; this is consistent with (8) if $\text{Mn}_2(\text{CO})_{10}$ is reformed from $\text{Mn}(\text{CO})_6$ by the stoichiometric process:



Polymerizations photoinitiated ($\lambda = 365$ nm) by $\text{Re}_2(\text{CO})_{10}$ show a long-lived after-effect, persisting for several hours at room temperatures after irradiation has been discontinued¹⁷. The after-effect, which is shown by several monomers, is quite distinct from (and much more pronounced than) that associated with the finite rate of normal free-radical decay. It does not originate in thermal initiation by $\text{Re}_2(\text{CO})_{10}$, which is extremely slow at 25°C ²². After-effects of this kind are not shown by systems containing $\text{Mn}_2(\text{CO})_{10}$ in the absence of additives (*vide infra*). Bamford, Crowe, Hobbs and Wayne¹⁷ proposed that the prolonged after-effects arise from reaction between $\text{Re}(\text{CO})_6$ formed in (8) and CCl_4 . Thus, with $\text{Re}(\text{CO})_6$, (9) is relatively slow, and the thermal reaction between $\text{Re}(\text{CO})_6$ and CCl_4 generates radicals

and so is responsible for the after-effect. On the other hand, $\text{Mn}(\text{CO})_6$ reacts rapidly according to (9), and little after-effect is observable. Supporting evidence for this view was provided by the observation²³ that a solution of $\text{Re}_2(\text{CO})_{10}$ in methyl methacrylate, after a short irradiation ($\lambda = 365 \text{ nm}$) and subsequent standing in the dark for one hour, produces polymer when added to a mixture of monomer and carbon tetrachloride. (No significant polymerization occurs during irradiation.) With manganese carbonyl, intermediates formed on irradiation decayed much more rapidly. The divergent behaviour of the two systems may therefore originate in differences between the relative rates of reactions such as (9).

We may now consider the overall reaction scheme (10) which is based on these ideas.



Trichloromethyl radicals generated in (10c) are responsible for the initiation of polymerization; this was proved to be so by the work of Bamford, Eastmond and Robinson²⁴ in which the halide component was CCl_4 enriched with $^{14}\text{CCl}_4$. The major manganese product for short irradiation times is $\text{Mn}(\text{CO})_5\text{Cl}$, in accordance with the observations of Kwok¹⁹ and of Bamford, Burley and Coldbeck²⁵†. We distinguish between two cases: (i) in which reaction (10e) is first order, and (ii) in which (10e) is second order in $[\text{Mn}(\text{CO})_6]$. By assuming stationary concentrations of $\text{Mn}(\text{CO})_4$ and $\text{Mn}(\text{CO})_6$ we may derive the following relations if all $\dot{\text{C}}\text{Cl}_3$ radicals initiate polymerization. Case (i):

$$\frac{\omega}{I_{\text{abs}}^{\frac{1}{2}}} = \frac{k_p [\text{M}]}{k_t^{\frac{1}{2}}} \left(\frac{\alpha [\text{CCl}_4]}{2 I_{\text{abs}}} \right)^{\frac{1}{2}} \left\{ \left(1 + \frac{4k_1 I_{\text{abs}}}{\alpha [\text{CCl}_4]} \right)^{\frac{1}{2}} - 1 \right\}^{\frac{1}{2}} \quad (11)$$

Case (ii):

$$\frac{k_1 k_p^2 [\text{M}]^2 I_{\text{abs}}}{k_t \omega^2} - \frac{k_2 k_1^{\frac{1}{2}} \omega}{k_p k_3 k_4^{\frac{1}{2}} [\text{M}] [\text{CCl}_4]} + 1 = 0 \quad (12)$$

In these equations $\omega = -d[\text{M}]/dt$ is the rate of polymerization, k_p , k_t are the velocity coefficients for propagation and termination, respectively, and $\alpha = k_3 k_4 / k_2$. Bamford, Crowe and Wayne¹⁶ reported that (with $[\text{M}]$ constant) $\omega/I_{\text{abs}}^{\frac{1}{2}}$ is a function of the single variable $[\text{CCl}_4]/I_{\text{abs}}$. Equation (11) shows that this holds for Case (i); on the other hand, it is not valid for Case

† $\text{Mn}(\text{CO})_5\text{Cl}$ in methyl methacrylate solution readily undergoes ligand substitution with formation of $\text{Mn}(\text{CO})_3(\text{mma})_2\text{Cl}$ and $[\text{Mn}(\text{CO})_3(\text{mma})\text{Cl}]_2$. These transformations and the photochemical reactions of the complexes have been discussed by Bamford, Burley and Coldbeck²⁵. The latter processes are significant in the $\text{Mn}_2(\text{CO})_{10}/\text{CCl}_4$ system if irradiation is prolonged.

(ii) [equation (12)]. (We may note at this point that the simple mechanism comprising symmetrical fission (7), the reverse recombination of $2\text{Mn}(\text{CO})_5$ and a radical-generating reaction between $\text{Mn}(\text{CO})_5$ and CCl_4 does not predict the above relation. In this case $\omega/I_{\text{abs}}^\ddagger$ is determined by $[\text{CCl}_4]/I_{\text{abs}}^\ddagger$.)

Since the quantum yield of initiation is unity at high $[\text{CCl}_4]$, it follows that $k_1 = 1$. Equation (11), with $k_1 = 1$ and $\alpha = 2.5 \times 10^{-5} \text{ s}^{-1}$ is in reasonable agreement with the experimental data of Figs. 5, 6 ref. 16 (see Figure 2). Although equation (12) ($k_1 = 1$, $k_2/(k_3k_4^\ddagger) = 8.43 \text{ mol}^\ddagger \text{ l}^{-\ddagger} \text{ s}^\ddagger$) predicts the general pattern of the observations in Figure 2 quantitatively, it is less satisfactory than (11). We therefore conclude that the most satisfactory agreement with experiment is obtained if (10e) is a first-order process.

Although the $\text{Mn}_2(\text{CO})_{10}/\text{CCl}_4$ system does not give rise to marked after-effects with bulk monomer, prolonged after-effects are found in the presence of certain additives (S), notably cyclohexanone and acetylacetone; other ketones show some activity²⁶. The observed phenomena, which resemble those reported for $\text{Re}_2(\text{CO})_{10}/\text{CCl}_4$ systems, support the view that the primary photolysis occurs in an unsymmetrical fashion. Typical results showing the development of the after-effect are presented in Figure 3. No after-effect can be obtained unless the additive (S) is present during irradiation. On the other hand, the presence of monomer or halide is unnecessary, and the after-effect develops if a mixture of these compounds is added to a previously irradiated solution of $\text{Mn}_2(\text{CO})_{10}$ in S. It therefore appears that

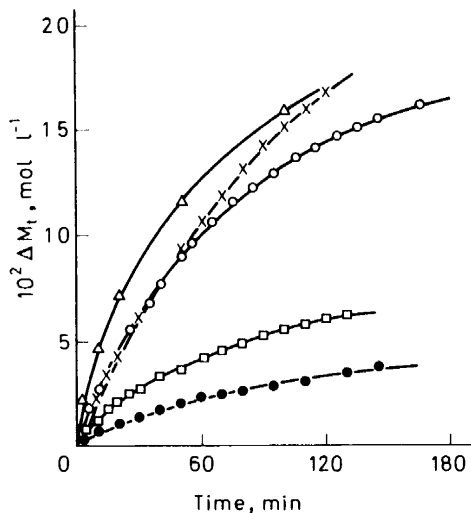
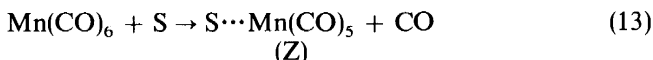


Figure 3. After-effects in polymerizations photoinitiated ($\lambda = 435.8 \text{ nm}$) by manganese carbonyl at 25°C . Irradiation for 5 min, interrupted at time zero in figure. ΔM_t —conversion (mol l^{-1}) at time t (min). $[\text{CCl}_3\text{COOEt}] = 6 \times 10^{-2} \text{ mol l}^{-1}$. Monomers—methyl methacrylate (MMA) and vinyl chloride (VC). Concentrations given below in mol l^{-1} : \bullet [MMA] = 4.7, $[\text{Mn}_2(\text{CO})_{10}] = 3.0 \times 10^{-4}$; solvent—benzene. \square [MMA] = 4.7, $[\text{Mn}_2(\text{CO})_{10}] = 2.1 \times 10^{-4}$; solvent—acetone. \circ [MMA] = 4.7, $[\text{Mn}_2(\text{CO})_{10}] = 3.9 \times 10^{-4}$; solvent—cyclohexanone. \times [MMA] = 4.7, $[\text{Mn}_2(\text{CO})_{10}] = 3.0 \times 10^{-4}$; solvent—acetylacetone. Δ [VC] = 8.6, $[\text{Mn}_2(\text{CO})_{10}] = 6.4 \times 10^{-4}$; solvent—cyclohexanone.

photochemical interaction between $\text{Mn}_2(\text{CO})_{10}$ and S produces a species (Z) capable of generating free radicals in a dark reaction with the halide. Spectrophotometric observations indicate the formation of a labile species with a half-life of several hours at 25°C during irradiation of manganese carbonyl in cyclohexanone; no corresponding species is detectable in cyclohexane solution.

The kinetic data have been interpreted²⁶ in terms of reactions (10a, c, d, e) together with (13), (14) representing the formation of Z and its reaction with the halide R—Cl, respectively:



[This work was carried out at 'high' halide concentration, so that reaction (10b) was insignificant, and was not included.] By making the assumptions that all the R· radicals formed in (14) initiate polymerization, that the decay of [Z] during the after-effect arises solely from (14) and that [RCl] is constant we may readily show that

$$\Delta[\text{M}]_t = \frac{2k_p}{k_t^{\frac{1}{2}}} [\text{M}] \left(\frac{n[\text{Z}]_0}{k} \right)^{\frac{1}{2}} (1 - e^{-kt/2}) \quad (15)$$

where $\Delta[\text{M}]_t$ is the conversion in the after-effect at time t after interrupting illumination, k is the first-order velocity constant for (14) and $[\text{Z}]_0$ is the concentration of Z existing at $t = 0$. The experimental data, such as those shown in *Figure 3*, conform well to (15), from which $n[\text{Z}]_0$ and k may therefore be estimated. Electron-spin-resonance observations indicate negligible formation of Mn^{II} during the after-effect, so that n may be taken as unity. On this basis absolute evaluation of $[\text{Z}]_0$ is possible. It turns out that $[\text{Z}]_0$ increases as the volume fraction of S increases, the maximum value approaching the total concentration of radicals $[\text{R}\cdot]_{\text{total}}$ arising from (10a, c) during irradiation. This result clearly supports the mechanism outlined; of the two photolytic products (produced in equal concentration), $\text{Mn}(\text{CO})_4$ yields radicals by (10c) and $\text{Mn}(\text{CO})_6$ yields Z through (13). Further, the rate of initiation during irradiation is not sensibly decreased by the presence of acetylacetone, showing that the latter does not deactivate an intermediate normally participating in photoinitiation. Thus the observations do not favour the symmetrical type of photolysis (7); this would predict a decrease in rate of initiation with increasing [S] and also a linear variation of $[\text{Z}]_0/[\text{R}\cdot]_{\text{total}}$ with [S], without the attainment of a finite limit as [S] is increased.

Hitherto we have implied that the monomer does not partake in the formation of a long-lived initiator. Inspection of *Figure 3* shows that this is not strictly true; although the after-effect in monomer plus benzene is relatively small, it is nevertheless much larger than a normal photochemical after-effect. Probably a species of the type Z is formed from the monomer in low concentration and/or of low activity.

Most of the quantitative work on the after-effect has been carried out with small light doses; prolonged irradiation leads to complications arising from

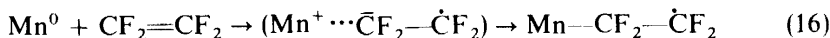
photolysis of Z. The reader may consult the original paper²⁶ for an account of this, and for further details of the kinetic treatment.

To summarize, the function of the additive in promoting the after-effect is to 'trap' the species $\text{Mn}(\text{CO})_6$, preventing its disappearance by (10e) and converting it into the derivative Z which, although relatively stable, is able to react with the halide and so initiate polymerization. We may note that the limiting overall quantum yield for radical generation, including radicals formed during irradiation and the after-effect, is two.

1.2 Other initiating systems based on transition metal complexes

Carbonyls of Groups VIIA and VIII

Initiation processes so far discussed involve electron-transfer to an organic halide with consequent rupture of a carbon-halogen bond. We may enquire whether any other mechanisms of radical generation exist in related systems. Bamford and Hughes²⁷ have shown that maleic anhydride (man) may replace halides in systems based on $\text{Ni}\{\text{P}(\text{OPh})_3\}_4$; these workers suggest that electron-transfer from $\text{Ni}\{\text{P}(\text{OPh})_3\}_3$ to (man), either by direct reaction or in the complex $\text{Ni}\{\text{P}(\text{OPh})_3\}_3(\text{man})$, leads to initiating radical anions $(\text{man})^\cdot$. However, in this system initiation is very inefficient. More recently, Bamford and Mullik²⁸ have demonstrated that manganese carbonyl is able to photosensitize ($\lambda = 435.8 \text{ nm}$) the polymerization of tetrafluoroethylene (TFE) in the absence of any other halide. The reaction occurs readily in bulk TFE or in carbon disulphide solution at -93°C . Tetrafluoroethylene may also be used instead of a conventional halide in $\text{Mn}_2(\text{CO})_{10}/\text{halide}$ systems: thus $\text{Mn}_2(\text{CO})_{10}/\text{TFE}$ can photosensitize ($\lambda = 435.8 \text{ nm}$) the free-radical polymerization of vinyl monomers such as methyl methacrylate, styrene and acrylonitrile at 25°C . The $\omega/[\text{TFE}]$ relation resembles the familiar halide curve (§1.1). Although TFE is considerably less active than CCl_4 , the plateau value in ω is attained for $[\text{TFE}] > 0.1 \text{ mol l}^{-1}$, approximately, and is the same as that obtained with CCl_4 . Saturated fluorocarbons such as perfluorocyclohexane are quite inactive. Rupture of a C—F bond at -93°C is most unlikely under these conditions, and initiation appears to be the result of electron transfer from a product of $\text{Mn}_2(\text{CO})_{10}$ photolysis [e.g. $\text{Mn}(\text{CO})_4$] to TFE, producing in the first place a radical anion and resulting ultimately in a species containing a Mn—C bond:



Further work on these new reactions is proceeding in an attempt to elucidate the nature of the products and to investigate the activities of other fluorine-containing derivatives.

We have studied photoinitiation ($\lambda = 365 \text{ nm}$) by osmium carbonyl $\text{Os}_3(\text{CO})_{12}$, and mention here a few points of interest²⁹. Osmium carbonyl resembles rhenium carbonyl¹⁷ in that polymerization of methyl methacrylate is initiated at an appreciable rate without addition of halide. We do not believe that this result is to be attributed to the presence of halide or other impurities in the monomer. Methyl methacrylate which has been saturated with $\text{Os}_3(\text{CO})_{12}$, irradiated for at least 6 h and distilled off, behaves in the same manner as the original monomer towards both $\text{Os}_3(\text{CO})_{12}$ and

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$\text{Re}_2(\text{CO})_{10}$. Addition of carbon tetrachloride leads to only moderate increases in the rate of initiation [Figure 4, curve (i)]; this halide curve may be contrasted with those for $\text{Mn}_2(\text{CO})_{10}$ in Figure 2. When osmium or rhenium carbonyls are irradiated ($\lambda = 365 \text{ nm}$) in cyclohexane solution, dicyclohexyl is formed, and infra-red examination of the osmium-containing products suggests the presence of osmium carbonyl hydrides. These findings are consistent with hydrogen-atom abstraction from cyclohexane by a photoexcited osmium species giving rise to cyclohexyl radicals which subsequently dimerize. It seems possible that hydrogen-atom abstraction from monomer is similarly responsible for initiation in the absence of halide.

A further unusual feature of photoinitiation by $\text{Os}_3(\text{CO})_{12}/\text{CCl}_4$ is shown in Figure 4 [curve (ii)], which indicates that the rate of initiation is markedly increased by addition of dimethylsulphoxide. Many other strong electron-donors behave similarly. No such effect is found with $\text{Mn}_2(\text{CO})_{10}/\text{CCl}_4$ systems. The overall polymerization has an order in [monomer] exceeding unity, showing that monomer is involved in initiation. Probably photolytic osmium carbonyl fragments are solvated by monomer before reaction with CCl_4 . Additional complex formation with electron-donors increases the rate of reaction with halide by further stabilization of incipient osmium cations. It is interesting that the rate of initiation in the absence of halide is decreased, not increased, by addition of dimethylsulphoxide, suggesting that initiation under these conditions does not involve a rate-determining electron transfer.

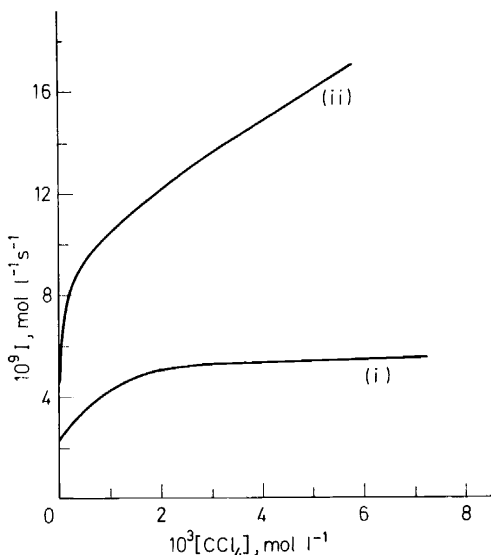


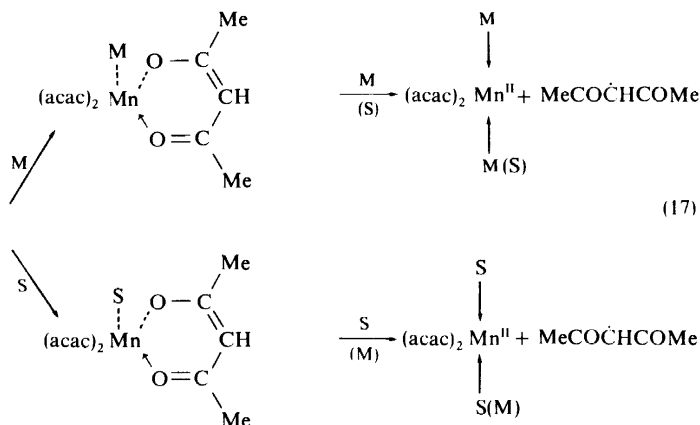
Figure 4. Photoinitiation ($\lambda = 365 \text{ nm}$) by $\text{Os}_3(\text{CO})_{12}$: dependence of rate of initiation \mathcal{I} on $[\text{CCl}_4]$ at 25°C . (i) $[\text{Os}_3(\text{CO})_{12}] = 2.01 \times 10^{-5} \text{ mol l}^{-1}$, bulk methyl methacrylate. (ii) $[\text{Os}_3(\text{CO})_{12}] = 2.25 \times 10^{-5} \text{ mol l}^{-1}$, 30 per cent methyl methacrylate plus 70 per cent dimethylsulphoxide (v/v).

Concluding remarks—Our discussion has shown that photoinitiation of free-radical polymerization by transition metal carbonyls may proceed by three routes, viz. (i) electron-transfer to an organic halide with rupture of a C—Cl or C—Br bond, (ii) electron-transfer to a strongly electron-attracting monomer such as C_2F_4 , probably without rupture of C—F, (iii) hydrogen-atom-transfer from monomer (or perhaps solvent) to a photoexcited metal carbonyl species. Of these (i) is the most frequently encountered.

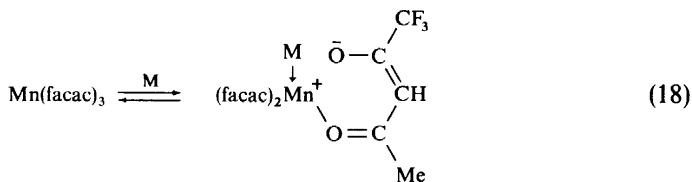
2. INITIATION BY TRANSITION METAL CHELATES

2.1 Thermal initiation

Many transition metal chelates can initiate free-radical polymerization under suitable conditions; of the simple chelates those of Mn^{III} have the highest activity³⁰⁻³². Manganic acetylacetonate $[Mn^{III}(acac)_3]$, for example, initiates at a convenient rate near $80^\circ C$. The reaction involves reduction of the chelate to $Mn^{II}(acac)_2$, with scission of a ligand as a free radical, which is the initiating species^{31, 32}. Monomer is involved in initiation, the order in $[M]$ being 1.5 in benzene and 1.2, approximately, in ethyl acetate³². The mechanism may be summarized by equation (17), in which S represents a solvent with electron-donating properties. There is no evidence that initiation is monomer-selective, initiation occurring at effectively the same rate in methyl methacrylate and styrene.



A different situation is encountered with manganese(III) 1,1,1-trifluoroacetylacetonate $[Mn^{III}(facac)_3]$. This chelate is much more active than $Mn(acac)_3$ in initiating the polymerizations of methyl methacrylate and acrylonitrile in the temperature range 60° to $80^\circ C$ but it is relatively inactive towards styrene and vinyl acetate. Indeed, a kinetic analysis suggests that no initiation occurs with styrene³². It has been suggested that the strong electron-attracting properties of the CF_3 group impose a polar route on the initiation process, the primary step being heterolytic [equation (18)] rather than homolytic as in (17).



If the monomer has a sufficiently high electron-accepting capacity (i.e. if it is readily susceptible to anionic polymerization) it may add to the anionic moiety in (18) (probably to C3) to give a monomer anion which is then oxidized by the Mn^{III} atom in the same molecule to produce an initiating radical³². These two processes may perhaps be more precisely described as monomer insertion followed by oxidation. They would clearly occur much more readily with methyl methacrylate and acrylonitrile than with the less polar monomers and could account for the high degree of monomer selectivity exhibited in initiation.

The rate of initiation by $\text{Mn}(\text{acac})_3$ is greatly augmented (in some cases up to 1000-fold) by the presence of donor additives such as dimethylsulphoxide (DMSO), 1,2-diaminopropane or aldehyde and ketones, so that these systems become active initiators at room temperatures³³⁻³⁶. Carboxylic acids also accelerate initiation³⁷. A full discussion of this aspect would not be in place here. We merely note that, at least with DMSO and the basic additives, some monomer selectivity of the type already discussed makes its appearance³⁶, and that the initiating species is a ligand radical^{34,36}. The salient experimental findings are consistent with an extension of the type of mechanism described above.

2.2 Photoinitiation

Relatively little attention has been paid to photoinitiation by chelates. We have investigated³⁸ the photochemistry of $\text{Mn}(\text{acac})_3$ and $\text{Mn}(\text{facac})_3$ in methyl methacrylate and styrene, and in mixtures of the former monomer with ethyl acetate and benzene. The absorption spectra of the two chelates are shown in *Figure 5*. Our work has been confined to $\lambda = 365$ nm, at which wavelength the extinction coefficients are $\text{Mn}(\text{acac})_3$ 2900, $\text{Mn}(\text{facac})_3$ 3700 $\text{mol}^{-1} \text{ l cm}^{-1}$. To avoid strong light absorption in kinetic studies, low chelate concentrations ($> 10^{-4} \text{ mol l}^{-1}$) and short path lengths were used.

Polymerizations of methyl methacrylate and styrene photoinitiated at 25°C by $\text{Mn}(\text{acac})_3$ show the normal kinetics of unretarded free-radical polymerizations, the rate being proportional to $[\text{M}]$, $[\text{Mn}(\text{acac})_3]^{\frac{1}{2}}$ (at constant incident intensity I_0) and $I_0^{\frac{1}{2}}$ (at constant $[\text{Mn}(\text{acac})_3]$). Similar results are obtained in benzene and ethyl acetate solutions. Rates of initiation under comparable conditions, calculated from rates of polymerization, are the same for the two monomers, hence no monomer selectivity is apparent. The quantum yield of initiation ϕ_i is low, approximately 8×10^{-3} .

Rates of chelate decomposition were measured spectrophotometrically at $\lambda = 350$ nm. The optical density decreases exponentially with time, corresponding to first-order chelate decomposition. In bulk monomer the

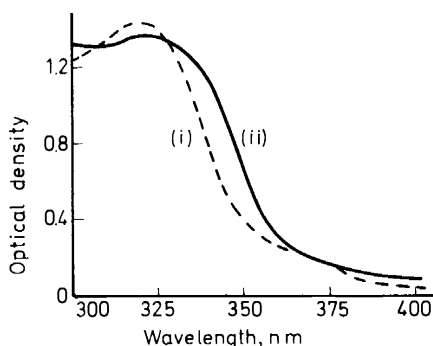


Figure 5. Near ultra-violet absorption spectra of Mn^{III} chelates: concentration $10^{-4} \text{ mol l}^{-1}$ in methyl methacrylate solution, path length 1 cm. (i) $\text{Mn}(\text{acac})_3$; (ii) $\text{Mn}(\text{facac})_3$. Spectra identical with those shown are also obtained with solutions in benzene, ethyl acetate and styrene.

first-order rate coefficient is proportional to I_0 and the quantum yield for decomposition $\phi_d = 2 \times 10^{-2}$, approximately. Surprisingly, the coefficient was found to depend linearly on the monomer concentration, as shown in Figure 6, the results again being independent of the nature of the diluent.

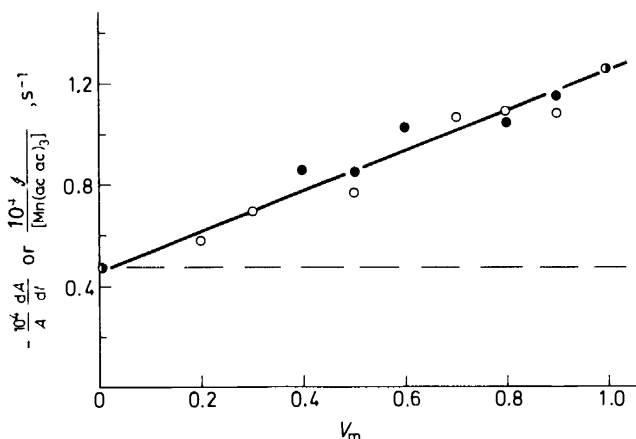


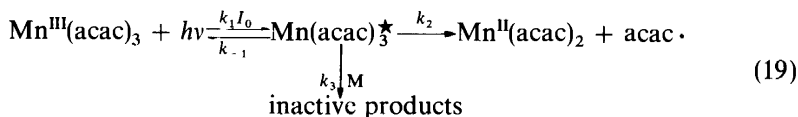
Figure 6. Photoinitiation ($\lambda = 365 \text{ nm}$) of polymerization of methyl methacrylate by $\text{Mn}(\text{acac})_3$ at 25°C . $I_0 = 1.00 \times 10^{-6} \text{ einstein l}^{-1} \text{ s}^{-1}$. — Dependence of first-order rate coefficient for decrease in optical density A at $\lambda = 350 \text{ nm}$ on volume fraction of monomer V_m : \circ ethyl acetate solution. \bullet benzene solution. ---- $\phi/[\text{Mn}(\text{acac})_3]$.

This diagram also indicates the independence of ϕ on $[\text{M}]$; although measurements of the rate of radical formation at $[\text{M}] = 0$ were not made, it appears that under these conditions it would equal the rate of chelate consumption.

These experiments illustrate the stability of the chelate ring towards photolysis; 97.9 per cent of the absorbed light causes no permanent chemical change. No fluorescence from the chelate could be detected in dilute (10^{-4} mol l^{-1}) solutions in benzene or methanol over a wide range of wavelengths.

The volatile products of photolysis of $Mn(acac)_3$ in benzene and cyclohexane were found to be biphenyl and bicyclohexyl, respectively, together with acetylacetone. Cyclohexene, if present, would not have been detected. These findings are consistent with primary formation of acetylacetyl radicals ($acac\cdot$) from the chelate, followed by hydrogen atom abstraction from the solvent, giving radicals which subsequently dimerize.

A simple mechanism which accounts for the observation is presented in (19).



The deactivation (k_{-1}) must be important in view of the low quantum yields. It may be a radiationless process or a cage recombination; the former seems preferable on chemical grounds. Distinction between the two might be possible if quantum yield measurements over a range of wavelengths were available. Reaction between $Mn(acac)_3^*$ and monomer (k_3) is included to allow for the enhanced rate of chelate decomposition in the presence of monomer. The nature of this reaction, which occurs with both monomers at the same rate, is obscure. It cannot involve polymer radicals since its rate is monomer-dependent. An overall process which is non-radical-forming is difficult to formulate without the assumption that two ligands become detached as radicals from the same chelate molecule, effectively simultaneously; in this event the radicals may add to the monomer molecule, the whole reaction occurring without escape of radical intermediates. The Mn^I product might subsequently disproportionate with Mn^{III} to yield Mn^{II} .

Using the approximation $k_{-1} \gg k_2, k_3[M]$, we obtain from (19):

$$\mathcal{J} = \frac{k_1 k_2}{k_{-1}} I_0 [Mn(acac)_3]$$

$$- \frac{d[Mn(acac)_3]}{dt} = \frac{k_1(k_2 + k_3[M])}{k_{-1}} I_0 [Mn(acac)_3] \quad (20)$$

$$\phi_i = k_2/k_{-1}$$

$$\phi_d = (k_2 + k_3[M])/k_{-1}$$

Comparison with the experimental data then yields the numerical values given in (21).

$$k_1 = 5940 \text{ mol}^{-1} \text{ l}; k_{-1}/k_2 = 126.4, k_{-1}/k_3 = 700 \text{ mol}^{-1} \text{ l} \quad (21)$$

It follows that, in bulk monomer, 37 per cent of the excited chelate molecules which react yield radicals by spontaneous decomposition.

The rate of polymerization of bulk methyl methacrylate photoinitiated by $Mn(facac)_3$ is proportional to $[Mn(facac)_3]^{\frac{1}{2}}$ at constant I_0 . Again, the

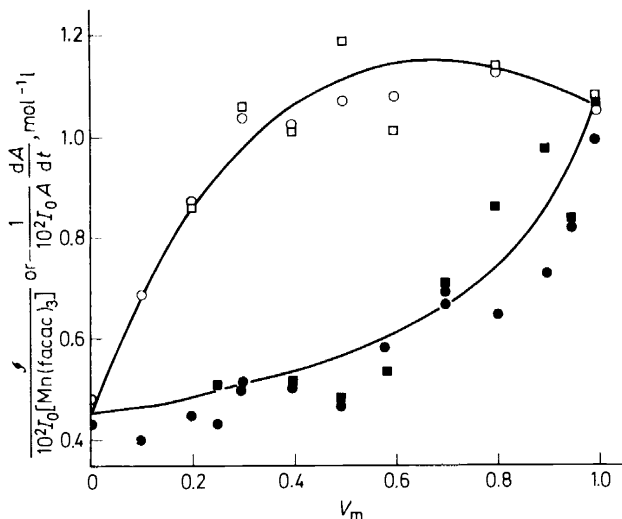


Figure 7. Photoinitiation ($\lambda = 365$ nm) of polymerization of methyl methacrylate by $\text{Mn}(\text{facac})_3$ at 25°C . Dependence of rate coefficients for photoinitiation and decrease in optical density A at $\lambda = 350$ nm on volume fraction of monomer V_m . \square , $\phi/([\text{Mn}(\text{facac})_3]I_0)$; \circ — $(dA/dt)/AI_0$ in ethyl acetate solution. \blacksquare , $\phi/([\text{Mn}(\text{facac})_3]I_0)$; \bullet — $(dA/dt)/AI_0$ in benzene solution.

quantum yield of initiation is low, 1.5×10^{-3} , approximately. In marked contrast to the results with $\text{Mn}(\text{acac})_3$, the rate of photoinitiation is subject to a pronounced solvent effect (Figure 7). Dilution of bulk monomer with an equal volume of ethyl acetate has little effect on the rate of initiation, whereas similar dilution with benzene almost halves the rate. Further, rates of chelate decomposition and rates of initiation are equal, within the limits of experimental error, over the whole range of composition (Figure 7). There is therefore no significant reaction leading to destruction of the chelate without radical formation and $\phi_i = \phi_d$.

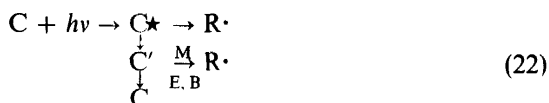
Polymerization of bulk styrene photoinitiated by $\text{Mn}(\text{facac})_3$ is complicated by strong retardation (compare Bamford and Lind³²). Rates of initiation and retardation may be estimated by a procedure similar to that used by Bamford and Lind³²; it turns out that the rate of initiation for bulk styrene is effectively the same as that for bulk methyl methacrylate. Monomer selectivity, which is such a pronounced feature in thermal initiation by $\text{Mn}(\text{facac})_3$ (§2.1), is therefore absent from photoinitiation.

The products of photolysis of the chelate in benzene and cyclohexane were found to be biphenyl and bicyclohexyl; 1,1,1-trifluoroacetylacetone was identified in the benzene solution, but could not be identified conclusively in the cyclohexane solution, probably on account of the low solubility of the chelate in this solvent. The primary decomposition under these conditions is therefore likely to be scission of a ligand as the free radical $\text{facac}\cdot$.

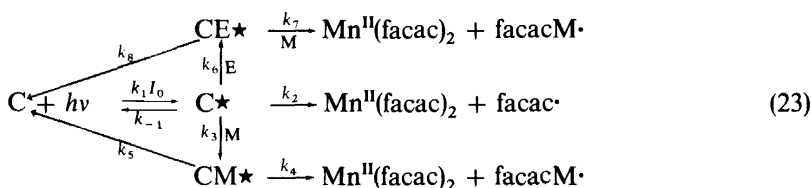
We now consider the mechanism of photoinitiation by $\text{Mn}(\text{facac})_3$. The solvent dependences shown in Figure 7 are unlikely to arise from reaction of either solvent (benzene or ethyl acetate) with initiating radicals; over the

greater part of the concentration range these radicals would be captured by monomer and would not react with solvent. Neither solvent has a significant effect on chain propagation. Thus deactivation of excited species by the solvents and the participation of monomer in radical generation are likely to be involved. Since the chelate (C) is photolysed at approximately the same rates in benzene and ethyl acetate solution, it is reasonable to suppose that direct deactivation by the solvents of the excited species formed by light absorption (C^\star) does not play a major role, unless these processes happen to be equally efficient in the two media. We therefore believe that the radiationless process $C^\star \rightarrow C$ is of predominating importance, as with $Mn(acac)_3$.

Inspection of the curves in *Figure 7* shows that methyl methacrylate enters into reactions leading to initiation and chelate decomposition. The results in the region close to $V_m = 0$ (V_m is the volume fraction of monomer) further suggest that an excited species may be involved which is rapidly deactivated by benzene, but less readily by ethyl acetate. We therefore investigated the simple scheme shown in (22) in which E, B represent ethyl acetate and benzene, respectively, and C' is an excited species arising from C^\star .



This scheme, however, does not provide a good fit to the experimental data. A more satisfactory mechanism is obtained by assuming that C^\star forms an exciplex CM^\star with the monomer, which may revert to $C + M$ or decompose into $facacM^\cdot$ radicals and $Mn^{II}(facac)_2$. This alone is inadequate, since it predicts a linear relation between \mathcal{J} and V_m , which is not observed. Since \mathcal{J} and $-d[C]/dt$ vary little over the range of V_m from 0.3 to 1.0 in ethyl acetate, we are led to believe that monomer and ethyl acetate are to some extent interchangeable in the reaction, and that E may also form an exciplex CE^\star . The complete mechanism is presented in (23).



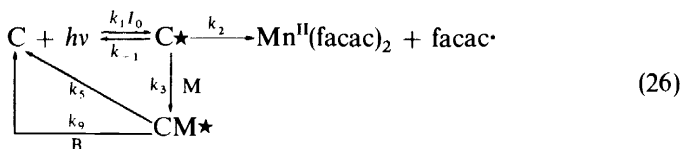
From this, with the assumption that $k_{-1} \gg k_2 + k_3[M] + k_6[E]$ we derive

$$\frac{\mathcal{J}}{[C]} = -\frac{1}{[C]} \frac{d[C]}{dt} = \frac{k_1 k_2}{k_{-1}} I_0 \left(1 + \frac{k_3 k_4 [M]}{k_2 (k_4 + k_5)} + \frac{k_6 k_7 [M][E]}{k_2 (k_8 + k_7 [M])} \right) \quad (24)$$

Curve (i) in *Figure 7*, which is a reasonable fit to the experimental data, has been calculated from (25), which has the same form as (24).

$$\frac{\mathcal{J}}{[C]} = -\frac{1}{[C]} \frac{d[C]}{dt} = 45 I_0 \left(1 + 0.145 [M] + \frac{[M][E]}{2(10 + [M])} \right) \quad (25)$$

The corresponding reaction scheme for benzene solutions is simpler and is shown in (26); the only additional reaction is deactivation of CM^\star by benzene.



From (26) we obtain

$$\frac{\mathcal{J}}{[\text{C}]} = -\frac{1}{[\text{C}]} \frac{d[\text{C}]}{dt} = \frac{k_1 k_2}{k_{-1}} I_0 \left(1 + \frac{k_3 k_4 [\text{M}]}{k_2 (k_4 + k_5 + k_6 [\text{B}])} \right) \quad (27)$$

and the related equation (28) is shown in *Figure 7* curve (ii) to agree reasonably well with the experimental data.

$$\frac{\mathcal{J}}{[\text{C}]} = -\frac{1}{[\text{C}]} \frac{d[\text{C}]}{dt} = 45 I_0 \left(1 + \frac{[\text{M}]}{6.9 + 2.1 [\text{B}]} \right) \quad (28)$$

The mechanisms we have proposed in (23), (26) have been shown to be in satisfactory accord with experiment; nevertheless, in view of their complexity they cannot be regarded as established by the available data. Further observations, if possible by different techniques, are clearly desirable.

General

The results described show that photolysis of $\text{Mn}(\text{acac})_3$ and $\text{Mn}(\text{facac})_3$ by light of $\lambda = 365 \text{ nm}$ yields ligand radicals which can initiate polymerization and abstract hydrogen atoms from hydrocarbons. We have represented these reactions as intramolecular photo-oxidation-reduction processes in equations (19), (23), (26), and we therefore believe they involve ligand \rightarrow metal charge transfer (LMCT) excited states. In this respect the reactions resemble the photolysis³⁹ of $[\text{Mn}^{\text{III}}(\text{C}_2\text{O}_4)]^{3-}$.

Barnum^{40,41} has suggested that the bands in the spectrum of $\text{Mn}(\text{acac})_3$ near 320, 390 nm correspond to $d_i \rightarrow \pi_4$ transition, i.e. they involve electron-transfer from metal to ligand. On this basis, excited states arising from absorption at $\lambda = 365 \text{ nm}$ are unlikely to be those leading directly to decomposition. Thus a radiationless transition to the reactive LMCT excited state may have to be assumed. Situations of this kind, in which there is no correlation between the primary excited state and the mode of reaction, are well recognized; an example is provided³⁹ by the photolysis of $[\text{Mn}^{\text{III}}(\text{C}_2\text{O}_4)]^{3-}$. Barnum⁴⁰ has also pointed out that several LMCT transitions (e.g. $\pi_3 \rightarrow d_i$) exist with energies less than 50000 cm^{-1} ($\lambda > 200 \text{ nm}$) and has argued against these being the origins of the bands mentioned. However, if they have low probabilities their presence may not be evident, although, in view of the low quantum yields, they may be involved in photolysis.

The differences between $\text{Mn}(\text{acac})_3$ and $\text{Mn}(\text{facac})_3$ as thermal initiators (mainly monomer selectivity) are not apparent in photoinitiation. However, other differences between the chelates emerge, notably the role assigned to exciplexes with $\text{Mn}(\text{facac})_3$.

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