

Solvent-trapping of Active Species in the Photolysis of Manganese Carbonyl

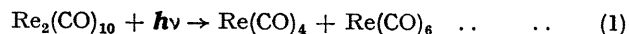
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Summary Photopolymerization of a vinyl monomer initiated by manganese carbonyl in association with ethyl trichloroacetate is followed by a prolonged after-effect if a suitable solvent is present, *e.g.*, acetylacetone or cyclohexanone; the observations are consistent with unsymmetric fission of $\text{Mn}_2(\text{CO})_{10}$ on photolysis, and subsequent reaction of one fragment $[\text{Mn}(\text{CO})_6]$ with solvent to give a species of relatively long life which generates radicals by reaction with the halide.

When rhenium carbonyl in association with carbon tetrachloride (or other active halogen compound) is used as photoinitiator of free-radical polymerization a prolonged

after-effect occurs when irradiation is interrupted.^{1,2} To account for this it has been suggested² that photolysis of the carbonyl leads to an unsymmetric scission [*e.g.*, reaction (1)]. One fragment, $\text{Re}(\text{CO})_4$, is considered to react



rapidly with the halide, generating radicals, while the other, being sufficiently stable to persist for a considerable period after irradiation, forms radicals relatively slowly, and is responsible for the after-effect. In similar circumstances (with bulk monomer) manganese carbonyl behaves differently,¹⁻³ giving only small after-effects little greater than those normally encountered in free-radical polymerization

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when initiation is abruptly terminated. We now report the existence of large after-effects following irradiation of $\text{Mn}_2(\text{CO})_{10}$ in the presence of certain solvents, notably acetylacetone (acac) and cyclohexanone (ch). Most of the work has been carried out with methyl methacrylate (mma) as monomer; the general pattern of the results is not dependent on the nature of the monomer, and similar behaviour is found with vinyl chloride.⁴ The halide component of the initiating system was ethyl trichloroacetate. Mixtures were irradiated with light having $\lambda = 4358 \text{ \AA}$; at this wavelength all components except $\text{Mn}_2(\text{CO})_{10}$ are transparent.

Typical results are shown in the Figure. Acetylacetone and cyclohexanone are "active" solvents and give rise to relatively large and prolonged after-effects, while benzene is inactive. A significant after-effect is obtained only if manganese carbonyl is irradiated in the presence of the active solvent; presence of monomer or halide is not necessary during irradiation, and the after-effect develops if these components are added subsequently. These conclusions follow from experiments of the types summarised in the Table; in all cases solutions were irradiated and mixed in evacuated vessels and reactions were followed dilatometrically. No photoreactions or after-effects can be observed in the absence of the halide.

Conditions necessary for the existence of a large after-effect
Final concentrations (M): $\text{Mn}_2(\text{CO})_{10}$ 3.2×10^{-4} ; mma 4.70 ;
ch 4.81 ; $\text{CCl}_3\text{CO}_2\text{Et}$ 6.5×10^{-2}

Mixture irradiated	Components added	After-effect
$\text{Mn}_2(\text{CO})_{10}$ + mma + ch	.. halide	+
$\text{Mn}_2(\text{CO})_{10}$ + ch mma + halide	+
$\text{Mn}_2(\text{CO})_{10}$ + mma mma + halide	-
$\text{Mn}_2(\text{CO})_{10}$ + mma ch + halide	-

It appears that interaction of the solvent with a normally short-lived product of photolysis of manganese carbonyl yields a species Z which is responsible for the after-effect. In the absence of halide, Z has appreciable stability; experiments similar to those in the Table, as well as spectrophotometric observations, show that the half-life of the species derived from cyclohexanone is *ca.* 7 h at 25°. Thermal reaction between Z and the halide generates free radicals and so gives rise to the after-effect. On the basis of this mechanism, the magnitude of the after-effect at time *t* after the end of irradiation is given by equation (2).

$$\Delta_t = \frac{2k_p[M]}{k_t^{\frac{1}{2}}} \left(\frac{[Z]_0}{k} \right)^{\frac{1}{2}} \{1 - \exp(-kt/2)\} \quad (2)$$

Here $[Z]_0$ is the concentration of Z at $t = 0$ and M represents monomer; k_p , k_t are the propagation and second-order termination coefficients, respectively, and k is the first-order constant for reaction of Z with the halide. The concentration of the latter is assumed to remain constant and each molecule of Z reacting is supposed to give one radical. In all cases the development of the prolonged after-effect conformed satisfactorily to equation (2). Since $[Z]_0$, k are the only unknowns, these quantities may be evaluated by fitting equation (2) to the experimental

data; the best fit was obtained by a computer programme which minimised the standard deviation. The total concentration of radicals formed during irradiation $[R\cdot]$ may readily be estimated from the rate of polymerization in the light. As the concentration of acetylacetone is

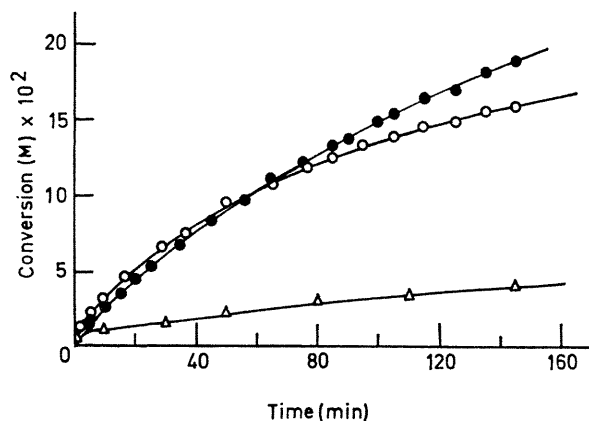


FIGURE. After-effects in methyl methacrylate polymerization at 25° photoinitiated ($\lambda = 4358 \text{ \AA}$) by $\text{Mn}_2(\text{CO})_{10} + \text{CCl}_3\text{CO}_2\text{Et}$. Period of irradiation 5 min. Conversion in light $3.5 \times 10^{-2}\text{M}$. Solvents: ● acetylacetone; ○ cyclohexanone; △ benzene in each case 50% bulk.
 $10^4[\text{Mn}_2(\text{CO})_{10}](\text{M})$: ● 2.97; ○ 3.90; △ 2.97.
 $10^2[\text{CCl}_3\text{CO}_2\text{Et}](\text{M})$: 6.5.

increased it appears that the ratio $[Z]_0/[R\cdot]$ approaches a limiting value close to unity. Further, provided the period of irradiation is not too long, $[R\cdot]$ is little affected by the presence of acetylacetone. The simplest mechanism consistent with these findings is unsymmetric fission of $\text{Mn}_2(\text{CO})_{10}$ as in reaction (1) followed by the trapping of one type of fragment [probably $\text{Mn}(\text{CO})_5$] by interaction with solvent to give species Z. This type of fission on photolysis has already been postulated by Bamford *et al.*^{2,3} for other reasons. Symmetric fission of $\text{Mn}_2(\text{CO})_{10}$ into $2\text{Mn}(\text{CO})_5$ followed by reaction between $\text{Mn}(\text{CO})_5$ and solvent does not seem acceptable since (i) it would predict that $[R\cdot]$ should decrease asymptotically to zero with increasing [solvent] and (ii) it offers no explanation of the approximate equality of $[Z]_0$ and $[R\cdot]$ at high [solvent]. This equality follows naturally from the unsymmetric mechanism, since each $\text{Mn}(\text{CO})_4$ formed in the light produces one radical. A mechanism in which photolysis occurs by two routes, one leading to the species responsible for the after-effect and the other to radical formation is not definitely excluded, although on this basis the equality of $[Z]_0$ and $[R\cdot]$ would be accidental. Kilner and Wojcicki⁵ have reported the formation of an unstable compound by interaction of $\text{Mn}(\text{CO})_5\text{Cl}$ and acetylacetone. However, $\text{Mn}(\text{CO})_5\text{Cl}$, although a product of the photolysis of $\text{Mn}_2(\text{CO})_{10}$ in the presence of a halide, does not play a part in the processes under consideration, since an after-effect is obtained when irradiation is carried out in the absence of halide (see Table).

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⁴ W. H. Atkinson, unpublished results.

⁵ M. Kilner and A. Wojcicki, *Inorg. Chem.*, 1965, 4, 591.