# Photochemistry of the Carbonyls of Group VII Metals: Formation of Active Intermediates

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BOTH manganese carbonyl[1] and rhenium carbonyl[2] in the presence of carbon tetrachloride are efficient photosensitisers of vinyl polymerization. With rhenium carbonyl, but not with manganese carbonyl, as the sensitiser a long-lived photo-aftereffect is also observed. We have interpreted the kinetic data in terms of a primary photochemical process in which two fragments are formed from the metal carbonyl. One of these fragments may react rapidly with carbon tetrachloride to yield trichloromethyl radicals, the initiating species. The other fragment appears to react slowly (when it derives from rhenium carbonyl) or not at all (manganese carbonyl). The present communication describes investigations designed to demonstrate the existence of reactive intermediates in the photolysis of manganese and rhenium carbonyls.

The experiments were performed in glass vessels consisting of two limbs connected by a glass break-seal. One limb contained a solution of the metal carbonyl (usually in methyl methacrylate) and the other a solution of carbon tetrachloride. The solutions were thoroughly degassed, and the carbonyl solution irradiated for an appropriate period. The seal was then broken, the carbon tetrachloride solution poured into the carbonyl solution and any polymer produced precipitated into methanol and determined gravimetrically. The solution-mixing technique was found to be critical and a standard procedure was evolved which gives reproducible results. It is doubtful, however, whether this simple technique can give results of kinetic significance in these systems, and we prefer to regard the deductions as qualitative in nature.

Preliminary investigations showed that polymer is indeed formed if carbon tetrachloride is added to the irradiated carbonyl–monomer mixture. Blank tests showed that no polymer is formed if the solutions are not irradiated. These early experiments further indicated that longer periods of irradiation produce greater yields of polymer. For subsequent experiments, therefore, we chose a single convenient period of exposure to light (20 minutes for manganese carbonyl samples, 60 minutes for rhenium carbonyl). We consider first the results for manganese carbonyl. The solutions were mixed and allowed is stand in the dark: Figure 1 shows the variation of polymer yield with dark time. The yield reaches a limiting value of about 9 mg., and it seems that the limitation can arise in the following way. If the solutions are allowed to stand in the dark after irradiation, but *before* mixing, then the amount of polymer formed is reduced considerably: after ten minutes standing no polymer at all can be precipitated. It is clear that the intermediate which reacts with carbon tetrachloride to initiate polymerization decays comparatively rapidly. The yield of polymer in experiments in which mixing takes place

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[1] C. H. Bamford, P. A. Crowe, and R. P. Wayne, *Proc. Roy. Soc.*, 1965, *A*, **284**, 455.
[2] C. H. Bamford, P. A. Crowe, J. Hobbs, and R. P. Wayne, in preparation.

immediately after irradiation might, therefore, be expected to reach a limit after about ten minutes reaction time.

We investigated the possible intervention of monomer by irradiating a solution of manganese carbonyl in benzene for 60 min., and then adding a solution of carbon tetrachloride in methyl methacrylate; 9·4 mg. of polymer was subsequently precipitated.

Irradiated rhenium carbonyl–monomre solutions also yield polymer on the addition of carbon tetrachloride. The results obtained are shown in Table 1.

TABLE I

*Yields of polymer resulting from the irradiation of rhenium carbonyl–methyl methacrylate*

| Experiment | Time in dark (before seal is broken) (min.) | Time allowed to stand after mixing (min.) | Polymer yield (mg.) |
|---|---|---|---|
| 1 | Seal intact | 0 | 15·7 |
| 2 | Seal intact | 120 | 14·2 |
| 3 | 0 | 0 | 14·1 |
| 4 | 0 | 10 | 20·2 |
| 5 | 0 | 30 | 41·0 |
| 6 | 0 | 60 | 87·9 |
| 7 | 0 | 120 | 175·0 |
| 8 | 60 | 120 | 97·2 |
| 9 | $CCl_4$ present before irradiation | 120 | 264·3 |

Time of irradiation: 60 minutes.
$[Re_2(CO)_{10}]$: 2·0 mg. in 2·5 ml. methyl methacrylate.
$[CCl_4]$: 0·2 ml. in 2·3 ml. methyl methacrylate.

The first two experiments indicate that a small amount of polymer is formed during irradiation even in the absence of carbon tetrachloride, although no further polymerization occurs in the dark. These observations are in agreement with our kinetic data,[2] where the absence of carbon tetrachloride results in photo-initiation of low efficiency and no long-lived after-effect. Experiments (3) to (7) show that, after addition of carbon tetrachloride, polymer is formed in relatively high yield over about two hours; this yield is approximately 70% of that obtained when carbon tetrachloride is present before irradiation (9). Experiment (8) demonstrates that for rhenium carbonyl the rate of decay of the active intermediate is relatively slow.

An experiment in which a solution of rhenium carbonyl in benzene was irradiated for 60 min., and a solution of carbon tetrachloride in methyl methacrylate then added immediately, yielded 11·4 mg. of polymer. This is strong confirmation of the hypothesis that an active intermediate is formed on irradiation of the metal carbonyl in inert solvents as well as in monomer.

The results are consistent with a primary photochemical process in which the metal carbonyl is decomposed to one or more reactive intermediates. In the case of rhenium carbonyl, the intermediate persists for periods of the order of hours, and this is in agreement with our observations[2] that polymerization may occur for a similar period after irradiation has ceased.

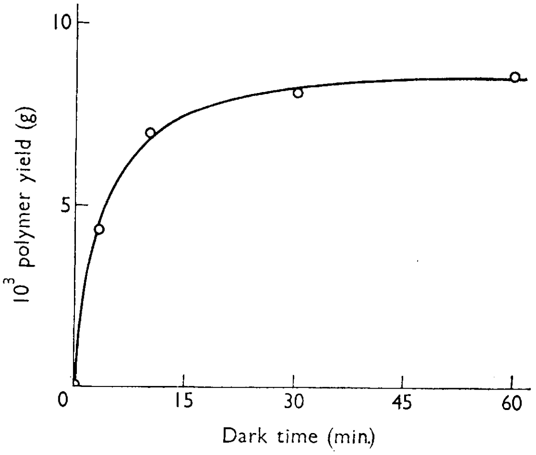

FIGURE 1

*Variation of polymer yield with time in the dark after mixing (a) and (b).*

(a) $Mn_2(CO)_{10}$ (0·5 mg.) in methyl methacrylate (2·5 ml.) irradiated for 20 min. at 25°.

(b) $CCl_4$ (0·2 ml.) with methyl methacrylate (2·3 ml.).

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