Photoinitiation of Polymerization and Hydrogen Abstraction by Metal Carbonyls

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Summary $Os_3(CO)_{12}$ and $Re_2(CO)_{10}$ when irradiated by light of $\lambda = 365$ nm initiate the polymerization of methyl methacrylate and acrylonitrile in the absence of organic halide; species arising from photoexcitation of the carbonyls are shown to abstract hydrogen from hydrocarbons to form the corresponding free radicals, and it is suggested that similar hydrogen abstraction from monomer is the origin of photoinitiation under the present conditions.

CARBONYLS and other derivatives of transition metals in a low oxidation state are normally employed as photo- and thermal initiators of free-radical polymerization in the presence of an organic halogen-containing compound. Usually the rate of initiation increases rapidly as the halide concentration [H] increases from zero, but ultimately reaches a plateau value independent of [H]. An example[1] is presented in the Figure (curve 1) which refers to the polymerization of methyl methacrylate photosensitized ($\lambda = 435{\cdot}8$ nm) by $Mn_2(CO)_{10}/CCl_4$.

We have recently observed that photoinitiation by triosmium dodecacarbonyl ($\lambda = 365$ nm) shows different characteristics. The Figure (curve 2) indicates that there is an appreciable rate of initiation in the absence of halide, and that addition of CCl_4 produces only relatively small increases. We believe that these results are not influenced by the presence of traces of halide or other impurities in the monomer for the following reason. A saturated solution of $Os_3(CO)_{12}$ in methyl methacrylate previously purified by standard methods, including prepolymerization,[2] was irradiated for 6 h, during which time about 10% conversion occurred. The residual monomer, removed by vacuum distillation, gave results indistinguishable from those in the Figure, curve 2.

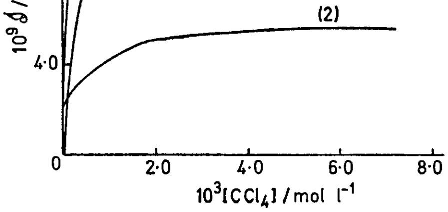

FIGURE. *Dependence of rate of photoinitiation* $\mathscr{I}$ *on carbon tetrachloride concentration at* 25 °C. (1) $Mn_2(CO)_{10}$, $5{\cdot}14 \times 10^{-5}$ mol l^{-1}, $\lambda = 435{\cdot}8$ nm, *bulk methyl methacrylate; taken from Figure* 5, *curve* (*c*) *of ref.* 1. (2) $Os_3(CO)_{12}$, $2{\cdot}01 \times 10^{-5}$ mol l^{-1}, $\lambda = 365$ nm, *bulk methyl methacrylate.* (3) $Os_3(CO)_{12}$, $2{\cdot}25 \times 10^{-5}$ mol l^{-1}, $\lambda = 365$ nm, 30% *methyl methacrylate* 70% *dimethyl sulphoxide* (v/v). *Curves* (2) *and* (3) *intersect the ordinate at* $10^9\mathscr{I} = 2{\cdot}3$ *and* $0{\cdot}6$ mol l^{-1} s^{-1}, *respectively.*

A significant rate of polymerization in the absence of halide was also observed with acrylonitrile in dimethyl sulphoxide solution.

Bamford *et al.*[3] remarked that in photosensitization by dirhenium decacarbonyl ($\lambda = 365$ nm) "the concentration of carbon tetrachloride required to reach the limiting light rate is exceedingly small, and unless very rigorous precautions are taken sufficient impurity is present in the monomer to give the limiting light rate". However, we have found that purification of methyl methacrylate by the method described above has no effect on the rate of photoinitiated polymerization obtained without addition of CCl_4. No observable rate could be obtained with dimanganese decacarbonyl ($\lambda = 365$ nm).

A series of experiments was carried out in which $Os_3(CO)_{12}$, $Re_2(CO)_{10}$, and $Mn_2(CO)_{10}$ were irradiated ($\lambda = 365$ nm) in cyclohexane solution. All three carbonyls gave rise to the formation of bicyclohexyl, identified by gas–liquid chromatography. Similar results were obtained when the cyclohexane was first submitted to prolonged shaking with concentrated sulphuric acid followed by washing with aqueous sodium hydroxide and water, drying and fractionating. Irradiation of cyclohexane alone produced insignificant quantities of bicyclohexyl. These experiments are consistent with hydrogen abstraction from cyclohexane by the photoexcited species, leading to cyclohexyl radicals which subsequently dimerize. This process might be expected to lead to hydrido-derivatives of osmium carbonyl.

Johnson *et al.*[4] have described the preparation of osmium carbonyl hydrides by interaction of $Os_3(CO)_{12}$, potassium hydroxide in methanol and phosphoric acid. Using this method we obtained a mixture of hydrides [formulated[4] as $H_2Os_3(CO)_{10}$, $HOs_3(CO)_{10}OH$, $H_2Os_4(CO)_{13}$, and $H_4Os_4(CO)_{12}$] which we were unable to separate. We compared the i.r. spectrum of the mixture with that of the osmium products obtained by irradiation of $Os_3(CO)_{12}$ in cyclohexane and removal of all volatile products in vacuum. The latter showed bands at 2080, 2060, 2055, 2025, and 2015 cm^{-1} which are not present in the original $Os_3(CO)_{12}$; these bands were also present in our hydride mixture, and are close to bands reported[4] in different hydride species.

These experiments indicate that photoinitiation of polymerization by the carbonyls in the absence of halide can occur through hydrogen abstraction from the monomer. This is consistent with another unusual feature of photoinitiation by $Os_3(CO)_{12}/CCl_4$. The reaction is strongly accelerated by the presence of electron-donors such as dimethyl sulphoxide and pyridine (Figure, curves 2 and 3). We attribute this behaviour to stabilisation by the additive of a cationic osmium species arising from electron transfer to the monomer and/or halide. (An account of this work will be published later.) No similar effect is encountered in the absence of carbon tetrachloride; this result would be expected if electron-transfer processes are not involved in rate-determining steps under these conditions.

It remains to explain why no polymerization was observed in the experiments with dimanganese decacarbonyl described above. An irradiated solution of this carbonyl in cyclohexane was added to methyl methacrylate containing the conventional initiator azobisisobutyronitrile in the absence of oxygen. No polymerization was obtained over a period of 6 h at 25 °C, although in a comparable experiment in which cyclohexane was added polymerization was detected in a short time. Evidently the manganese products of photolysis in the absence of halide are powerful retarders of polymerization and failure to observe polymerization does not necessarily imply that no initiation occurs.

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