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“Solvent-Free” Impregnation of Dinuclear Metal Complexes into Polyethylene: Use of Supercritical CO_2 and the *in Situ* Photochemical Assembly of $Mn_2(CO)_{10}$ from $HMn(CO)_5$

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Introduction

There is considerable interest in the use of polymer films impregnated with organometallics as matrices for photochemical studies. Rest and co-workers, in particular, have demonstrated some of the possibilities of this technique[1] including the study of compounds too involatile for conventional noble gas matrix isolation. In this context, polyethylene (PE) is attractive as a matrix material since, chemically, it is more inert than many other polymers.[2] Furthermore, anisotropic stretching of a PE film provides a simple method of orienting molecules within a solid matrix.[3] Sometimes, an organometallic compound will have sufficient vapor pressure to impregnate PE directly from the gas phase,[2a] but more frequently, the compounds are too involatile and a solvent must be used. However, the use of a solvent introduces the complication of residues in the polymer film, residues which can be hard to remove and which can give rise to unwanted chemical effects.

Recently, we showed that such problems can be overcome by the use of supercritical CO_2 ($scCO_2$) as the solvent for impregnation because the gaslike nature of a supercritical fluid greatly increases the rates of diffusion in and out of the polymer. We have found that impregnation becomes increasingly difficult as the crystallinity of the PE increases. Thus, low-density PE is more easily impregnated than the more crystalline high-density PE, which is particularly useful as an inert medium for photochemical reactions since it contains fewer olefinic C=C bonds than low-density PE. Nevertheless, we have successfully used $scCO_2$ to impregnate $Cp^*Ir(CO)_2$ into high-density PE without leaving any solvent residues; subsequent UV irradiation led to C–H activation of the polymer by the Ir center.[2b,c] Very recently, we have used FTIR to study the kinetics of supercritical impregnation of PE,[4,5] which is surprisingly fast and uniform on a scale of 100 μm.

Supercritical impregnation has worked well with a range of mononuclear metal complexes,[4] but it is quite slow for impregnation of dinuclear complexes such as $Mn_2(CO)_{10}$ even into low-density PE. It is the purpose of this note to show how $scCO_2$ can be used to assemble $Mn_2(CO)_{10}$ *in situ* within a high-density PE matrix. Our method is based on the photochemical reaction of $Mn_2(CO)_{10}$ with H_2, first reported by Brown and co-workers.[6] This reaction leads to formation of $HMn(CO)_5$, which is small enough to impregnate into PE. UV irradiation of $HMn(CO)_5$ in the presence of CO then allows $Mn_2(CO)_{10}$ to be regenerated, but now inside the PE matrix.

Results and Discussion

We have previously shown[7] that supercritical fluids are particularly suitable solvents for reactions involving H_2 because the complete miscibility of H_2 gives a much higher concentration of “dissolved” H_2 than could be obtained in a conventional solvent under similar conditions, an effect which has since been expoited by others.[8] The solubility of solids in supercritical solvents increases with increasing pressure and hence density.[9] $Mn_2(CO)_{10}$ is soluble in $scCO_2$ even at relatively low pressures, and the addition of a high pressure of H_2 has little effect on the solubility. The IR spectra in Figure 1 illustrate key stages in our *in situ* assembly of $Mn_2(CO)_{10}$ in PE.

(a) UV photolysis of a solution of $Mn_2(CO)_{10}$ in $scCO_2/H_2$ in a cell containing a disk of PE film with IR monitoring is used to follow the generation of $HMn(CO)_5$, some of which diffuses into the PE film. On releasing the pressure, the supercritical solution vents from the cell much more rapidly than either CO_2 or $HMn(CO)_5$ can diffuse out of the PE film. The CO_2 then diffuses out of the PE film after the pressure has dropped but the $HMn(CO)_5$ is left impregnated in the film (ν(C–O) 2028, 2014 cm^{-1}), Figure 1a.

(b) UV irradiation of such an impregnated film under a high pressure of CO leads to the destruction of $HMn(CO)_5$ and the regeneration of $Mn_2(CO)_{10}$; see Figure 1b.

$$2HMn(CO)_5 \overset{UV}{\rightleftharpoons} Mn_2(CO)_{10} + H_2$$

$HMn(CO)_5$ is not soluble in CO gas at this pressure and temperature, but CO diffuses into the PE. The photochemical reaction, therefore, takes place within the film. The role of CO is probably to suppress formation of the transient species $HMn(CO)_4$, and indeed, UV irradiation of the impregnated film in the absence of CO results in rapid decomposition of $HMn(CO)_5$ with little formation of $Mn_2(CO)_{10}$. Such suppression of $HMn(CO)_4$ by CO has been observed in cryogenic matrices[10] where high concentrations of CO favor formation of $Mn(CO)_5$.

(c) The CO is vented and $Mn_2(CO)_{10}$ is left impregnated in the PE, Figure 1c, with ν(C–O) bands, almost identical to those in C_6H_{12} solution[11] but slightly broader.

Similar results were obtained with high-density PE (Hostalen GUR 415), but the total amount of $Mn_2(CO)_{10}$ impregnated into the film was less than into low density PE of the same thickness. IR spectra recorded with plane polarized light confirm that the molecules of $Mn_2(CO)_{10}$ are randomly oriented within the film relative to laboratory-fixed axes. Equally, the distribution of $Mn_2(CO)_{10}$ throughout the thickness of the low-density PE film appears to be relatively uniform. For example, mechanical abrading of the surface with carborundum paper results in a reduction in the intensity of the bands consistent with the reduction in thickness of the film. Abrading also causes a somewhat greater reduction in intensity in the “wings” of the bands possibly due to removal of trace amounts of crystalline $Mn_2(CO)_{10}$ close to the surface in the initial stages of the abrasion.[12] The absorbance of the ν(C–O) bands in Figure 1c suggests that the concentration of $Mn_2(CO)_{10}$ in the film would be ca. 10^{-2} M, if $Mn_2(CO)_{10}$

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[1] For a recent example, see: Campen, A. K.; Rest, A. J.; Yoshihara, K. *J. Photochem. Photobiol., A: Chem.* **1991**, *55*, 301.

[2] (a) See e.g.: Burdett, J. K.; Grzybowski, J. M.; Perutz, R. N.; Poliakoff, M.; Turner, J. J.; Turner, R. F. *Inorg. Chem.* **1978**, *17*, 147; (b) Jobling, M.; Howdle, S. M.; Poliakoff, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1762; (c) Cooper, A. I.; Kazarian, S. G.; Poliakoff, M. *Chem. Phys. Lett.* **1993**, *206*, 175.

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[5] Cooper, A. I.; Hughes, C.; Howdle, S. M.; Johnston, K. P.; Kazarian, S. G.; Poliakoff, M.; Shepherd, L. A. *Analyst* **1993**, *118*, 1111.

[6] Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527.

[7] See e.g.: Howdle, S. M., Poliakoff, M. *J. Chem. Soc., Chem. Commun.* **1989**, 1099; Howdle, S. M.; Poliakoff, M.; Healy, M. A. *J. Am. Chem. Soc.* **1990**, *112*, 4804.

[8] Rathke, J. W.; Klingler, R. J.; Krause, T. R. *Organometallics* **1991**, *10*, 1350.

[9] See e.g.: McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction*, Butterworth: Boston, MA, 1986.

[10] Church, S. P.; Poliakoff, M.; Timney, J. A.; Turner, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 7515.

[11] ν(C–O) bands of $Mn_2(CO)_{10}$: C_6H_{12} solution, 2044, 2013, and 1983 cm^{-1}; impregnated PE film, 2044.5, 2012.1, and 1982.1 cm^{-1}.

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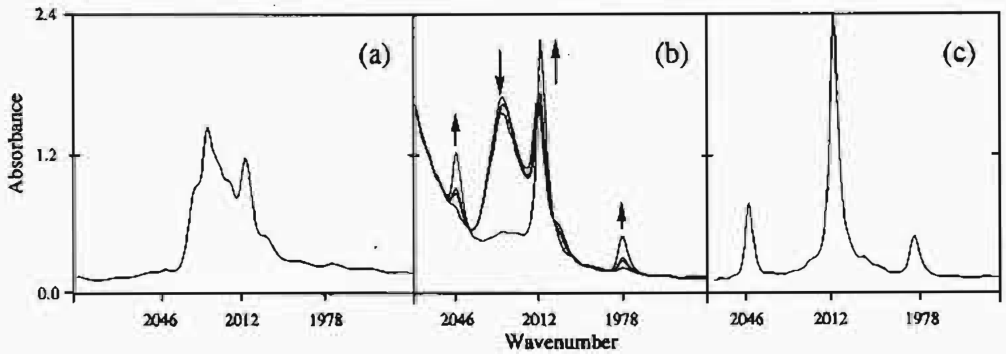

Figure 1. Sequence of IR spectra in the ν(C–O) region illustrating the various stages of impregnation of $Mn_2(CO)_{10}$ into low-density PE film. (a) $HMn(CO)_5$ impregnated into low-density PE film. The sample was obtained by venting the pressure, after 37-min UV photolysis of a solution of $Mn_2(CO)_{10}$ in $scCO_2$ (1635 psi) and H_2 (2988 psi total pressure). (b) Series of spectra recorded at intervals during UV irradiation of the impregnated film under a pressure of CO (800 psi). The band marked ↓, due to $HMn(CO)_5$, decreases in intensity on irradiation while those marked ↑, due to $Mn_2(CO)_{10}$, increase in intensity. The reaction is slow to go to completion; the first three spectra were recorded at intervals of ca. 5 min and the last spectrum was recorded after 115 min total irradiation time. (c) IR spectrum, obtained after venting the pressure of CO, showing the bands of $Mn_2(CO)_{10}$ impregnated into the PE film.

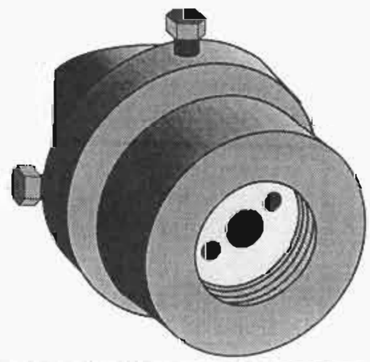

Figure 2. High pressure cell for use with supercritical fluids.

were distributed uniformly throughout both the crystalline and amorphous regions of the PE.

A similar method can be used to impregnate $Co_2(CO)_8$ into PE. UV irradiation of $Co_2(CO)_8$ in $scCO_2/H_2$ leads to the formation of $HCo(CO)_4$, which is stabilized by the high pressure of H_2. Subsequent UV irradiation of $HCo(CO)_4$ in PE leads to *in situ* formation of $Co_2(CO)_8$. Unlike $Mn_2(CO)_{10}$, $Co_2(CO)_8$ appeared to be particularly air-sensitive once impregnated into the PE film, decomposing rapidly even after brief exposure to air. $Co_2(CO)_8$ is well-known for the temperature-dependent equilibrium between the unbridged isomer and the thermodynamically more stable CO-bridged isomer.[13] We were therefore surprised to see little change in the ν(C–O) spectrum even when PE impregnated with $Co_2(CO)_8$ was cooled as low as 20 K. Presumably, the PE matrix becomes rigid as it is cooled, and this rigidity impedes the *bridged* $\rightleftharpoons$ *unbridged* interconversion.

Experimental Section

The high pressure cells for use with supercritical fluids, as illustrated in Figure 2, have been described in detail elsewhere.[14] CO_2 (Air Products, SFC grade) was compressed with a Lee Scientific Model syringe pump. PE (commercial film or Aldrich, low density, spectroscopic grade), $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ (Strem), and H_2 (Air Products) were used without further purification. A Cermax 300-W UV illuminator with Lumatec light guide was used for all photolyses. IR spectra were recorded on a Nicolet Model 730 interferometer and Model 680D Data station (2-cm^{-1} resolution).

Safety Note: *Caution! Supercritical experiments involve the use of relatively high pressures and should not be attempted without checking that the apparatus is suitably pressure-rated. Formulae for calculating the safe-operating pressures of spectroscopic windows can be found in Whyman's review.*[15]

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(12) Although the frictional heating associated with mechanical abrasion could cause changes to the polymer film, there was no evidence from the spectra that such changes were occurring in this case.

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