High-pressure reactions in polyethylene films, a new development in matrix isolation. The photochemical reaction of $Fe(CO)_5$ with N_2 and the thermal reaction of $Fe(CO)_4(N_2)$ with H_2

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A new miniature high-pressure cell has been developed for the spectroscopic study of reactions between organometallic compounds impregnated into polymer films and gases such as N₂ or H₂ at any temperature between ambient and 20 K. The use of the cell is illustrated by the photochemical reactions of Fe(CO)₅ in polyethylene film (PE) with N₂ and H₂ at 190 K to form Fe(CO)₄(N₂) and Fe(CO)₄H₂ respectively. IR spectra suggest that the N₂ group may occupy an equatorial rather than an axial position. Once formed, Fe(CO)₄(N₂) is shown to react thermally with H₂ at ≈ 210 K to yield the dihydride compound, Fe(CO)₄H₂.

1. Introduction

Reactions between transition metal compounds and gases such as CO or H_2 are a recurrent feature of organometallic chemistry, particularly in catalytic processes, see, e.g., ref. [1]. Spectroscopic studies can, in principle, provide much of the information needed to identify intermediates and to unravel the mechanism of such reactions. In practice, however, such experiments are technically difficult and most current approaches have distinct limitations.

The majority of spectroscopic autoclaves are bulky and awkward to use below ambient temperatures [2]. Cryogenic matrices (e.g. solid N₂ or CO) are extremely successful but only over a very limited temperature range, typically <40 K, so that one can rarely observe thermal reactions of coordinatively saturated compounds [3]. In addition, such matrices are difficult to use with H₂ and, for all solid matrices, the gas cannot be changed once the matrix is formed. Hydrocarbon glasses have a much wider temperature range than frozen gas matrices but the cells used for glass experiments are not normally designed to withstand significant gas pressures see, e.g., ref. [4]. Liquefied noble gases, particularly Xe, have also been very effective for studying reactions with gases [5] but, once added to the solution, some gases (e.g. N_2 or CO) are very difficult to remove and precipitation of compounds from solution can also be a problem.

In this Letter, we describe the use of a miniature high-pressure cryogenic cell which allows reactions between organometallics and gases to be studied within polymer matrices. Several groups, particularly that of Rest, have demonstrated that polymer films impregnated with organometallics can be used for matrix isolation experiments over a very wide temperature range, from 20 K to ambient [6], for a more recent example see ref. [7], [8]. Very recently, we have shown [9] that polyethylene (PE) is sufficiently permeable to gases that it can be used to generate stable dinitrogen compounds within PE films at room temperature by UV irradiation, under a high pressure of N_2 , of an PE film previously impregnated with an organometallic compound,

$$CpMn(CO)_{3} + N_{2} \xrightarrow{UV} CpMn(CO)_{2}(N_{2})$$
$$+ CO \quad (Cp = \eta^{5} - C_{5}H_{5}).$$
(1)

Our new cell allows these low-temperature and high-

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pressure experiments to be combined. Fig. 1 illustrates the principle of the cell, which is small enough to be screwed into the cold station of a closed-cycle cooler of the type normally used for matrix isolation. The cell can remain permanently connected to an outside gas supply via capillary tubing, while in position on the cooler. The important features of the cell are:

(i) The cell can hold a polymer film under a pressure of gas (up to 200 atm) and this gas can be changed at any time during an experiment;

(ii) The cell is vacuum tight so that it can fit into the vacuum jacket of the matrix isolation equipment and can be cooled to cryogenic temperatures without loss of gas; to 20 K with N₂ which, of course, solidifies at this temperature and, currently, to ≈ 50 K with H₂ because of the greater heat leakage than with N₂.

(iii) The amount of organometallic compound within the polymer film can be adjusted or changed by supercritical impregnation or extraction at room temperature, merely by flowing supercritical $CO_2(scCO_2)$ over the polymer in situ in the cell while monitoring the process spectroscopically. We now illustrate the operation of the cell by the photochemical reaction of $Fe(CO)_5$ with N₂, see eq. (2) below, and the subsequent reaction of $Fe(CO)_4(N_2)$ with H₂,



Fig. 1. Schematic cross section of the high-pressure cell, vacuum jacket and cooler. The components are labelled as follows: P, the polymer film; G, the inlet and outlet pipes for the high-pressure gases (e.g. H_2 or N_2); C, the tip of the cold finger of the closed-cycle refrigerator; V, the vacuum surrounding the high pressure cell; IR/UV, the colinear light paths of the IR spectrometer beam and UV photolysis beams (the outer windows in this light path are KBr and the thicker high pressure inner windows, CaF₂). Safety Note: The cell design shown in this figure is purely schematic and does not constitute a scale drawing of equipment which could be used safely under these high pressure conditions.

$$\operatorname{Fe}(\operatorname{CO})_5 + \operatorname{N}_2 \xrightarrow{\operatorname{UV}} \operatorname{Fe}(\operatorname{CO})_4(\operatorname{N}_2) + \operatorname{CO}.$$
 (2)

The reaction of $Fe(CO)_5$ with N_2 was first studied by us many years ago using solid N_2 matrices at 20 K but the IR bands were so split by "matrix effects" that it was difficult to decide whether the N_2 group in $Fe(CO)_4(N_2)$ occupied an axial or equatorial position $[10,11]^{\#1}$. The Fc centre in $Fe(CO)_4(N_2)$ is coordinatively saturated but it was not possible in the matrix experiments to obtain any indication of the thermal stability of the compound. More recent attempts to study the reactions of $Fe(CO)_5$ in liquid noble gases have been disappointing because the system appears to be very sensitive to traces of O_2 and because of the formation of insoluble polynuclear products [13].

2. Experimental

These experiments were carried out using Hostalen GUR 415 polyethylene (Hoechst), a high molecular weight polymer with a low concentration of olefinic C-C bonds. Powdered Hostalen PE was hotpressed into discs, typically 250 µm thick using a Specac polymer Film-maker. Fe(CO)₅ was impregnated into the film under vacuum. This procedure frequently gave a loading of Fe(CO)₅ with IR absorptions in the ν (C-O) region too intense for convenient spectroscopic measurement. Thus, once the impregnated film had been installed in the high-pressure cell, excess $Fe(CO)_5$ was removed by extraction with scCO₂ ^{#2}. The cell was mounted on an Air Products Displex CS-202 cooler, merely replacing the standard window holder in our matrix isolation apparatus which has been described previously *3. All temperatures were monitored via the standard thermocouple attached to the cold tip of the Displex; trial measurements (e.g. the freezing point of N_2) suggest that only a small error is introduced by monitoring the temperature at this position rather on the cell. Full details of the cell will be given elsewhere [16]. N_2 and H_2 and SFC-grade CO₂ (Air Products) were

- of organometallics from PE, see ref. [14].
- *3 For recent descriptions, see ref. [13].

^{#1} For a relatively full history of Fe(CO)₄, see ref. [12].

^{#2} For more details of supercritical impregnation and extraction

used as supplied. A Philips HPK 125 W Hg arc with water filtering was used for photolysis. IR spectra were recorded on a Nicolet MX3600 interferometer with a Model 1280 data station (16K data points, 2 cm⁻¹ resolution). "Background" spectra were run at a variety of temperatures across the range with clean PE discs of the appropriate thickness. Safety note: these experiments involve the use of high pressures and should be approached with due caution.

3. Results

Fig. 2 shows the IR spectrum of $Fe(CO)_5$ isolated



Fig. 2. IR spectra in the $\nu(C-O)$ and $\nu(N-N)$ regions showing (a) Fe(CO)₅ impregnated in PE and (b) the effects of UV photolysis at 190 K of the *same* sample under a pressure of N₂(950 psi \approx 6.5 MPa); the individual spectra correspond to total irradiation times of 1, 10, 30 and 60 min respectively and the high wavenumber region of the final spectrum is also shown with a \times 20 expansion of the absorbance scale. Bands are labelled as follows 4, Fe(CO)₅; †, Fe(CO)₄(N₂) and uncoordinated CO; (*) trace amounts of a polynuclear product (see text).

in PE film. The spectrum is similar to that previously reported for Fe(C), in low-density PE [6] with bands (2021.7 and 1998.3/1995.6 cm⁻¹, plus a very weak feature at 2030 cm^{-1}) somewhat broader than in fluid solution and, at these temperatures, with incipient splitting of the e band. UV irradiation of Fe(CO), in low-density PE at 20 K is known to promote photoejection of CO and formation of Fe(CO)₄ [6]. UV irradiation ($\lambda < 290$ nm, Cl₂ gas filter) in our cell at 190 K under pressure of N₂ leads to a reduction in the intensity of the bands of $Fe(CO)_5$ and the growth of new bands, arrowed in fig. 2b, close in wavenumber to those assigned to matrix-isolated $Fe(CO)_4(N_2)$. UV photolysis also causes the appearance of a very weak band at 2131 cm⁻¹, due to uncoordinated CO, see fig. 2b. The overall yield of $Fe(CO)_4(N_2)$ is comparable to that observed on photolysis of $Fe(CO)_5$ in solid Ar doped with 5% N₂ at 20K [10].

Fig. 3 shows the spectrum of $Fe(CO)_4(N_2)$ obtained by computer subtraction of the bands of unreacted $Fe(CO)_5$. The spectrum shows five bands (2235±2, 2083.3, 2006.8, 1981.6 and 1971.7 cm⁻¹), much broader than those in N₂ matrices but *without* the splitting which prevented the structural inter-



Fig. 3. IR difference spectrum obtained by a scaled computer subtraction (spectrum after UV minus spectrum before) to remove the bands of Fe(CO)₅, showing the ν (N-N) and ν (C-O) bands of Fe(CO)₄(N₂). Other features are labelled; (*) trace amounts of a polynuclear product (see text); (×) artefacts arising from incomplete cancellation of the bands of Fe(CO)₅. Note that this spectrum was obtained in an experiment, separate but almost identical from that illustrated in fig. 2.

pretation of the matrix spectra [10-12]. The relative intensities of the bands are reminiscent of the $\nu(C-O)$ bands of $Mn(CO)_4(NO)$, which has NO in the equatorial position and are quite different from those of PH₃Fe(CO)₄, which has PH₃ in an axial position. Thus, the spectra suggest that, probably, Fe(CO)₄(N₂) has an equatorial N₂ rather than an axial N₂ group with C_{2v} rather than C_{3v} symmetry, a conclusion which could not be drawn from the original matrix spectra.



Our spectra show no trace of bands assignable to the $Fe(CO)_4$ (polymer) species, which have been reported previously to be formed by photolysis of $Fe(CO)_5$ in low-density PE [6]. The absence of $Fe(CO)_4$ (polymer) in these experiments is due to the nature of Hostalen PE which has far fewer olefinic C-C bonds than does low-density PE. Work in our laboratory with a range of metal carbonyls has shown that only trace amounts of $M(CO)_x$ - $(\eta^2-C=C)$ complexes are formed on photolysis at room temperature in Hostalen PE compared to the amounts formed in low-density PE under similar conditions [17]. On the other hand, there is a weak band (2054.8 cm^{-1}), marked with an asterisk in figs. 2b and 3, which is not due to either $Fe(CO)_5$ or $Fe(CO)_4(N_2)$ and which can be assigned to a polynuclear product of the following grounds; (a) the intensity of this band and that of an associated band at ≈ 1825 cm⁻¹, increase relative to those of $Fe(CO)_4(N_2)$ with increasing initial concentration of $Fe(CO)_5$ in the polymer and (b) these bands are also more intense when the photolysis is carried out at higher temperatures where diffusion of $Fe(CO)_5$ through the polymer matrix will be easier and (c) the 1825 cm^{-1} band lies in the wavenumber region normally associated with bridging CO groups. Since only two bands are observed it is not possible to distinguish between $Fe_2(CO)_8$ and $Fe_3(CO)_{12}$, both of which are known to have bands close to these frequencies [18,19]. Perhaps $Fe_3(CO)_{12}$ is the more

likely because, in Ar matrices, the bridged isomer of $Fe_2(CO)_8$ undergoes isomerization to the unbridged form merely by warming to 40 K [18].

At 190 K, Fe(CO)₄(N₂) is stable in the PE matrix under 1000 psi pressure of N₂ for more than 1 h. There appears to be little reaction even when the N₂ gas replaced by a similar pressure of H₂ until the temperature is raised to 210 K. At this temperature, there is a smooth conversion of Fe(CO)₄(N₂) to a new product with three distinct ν (C-O) bands to higher wavenumber (2116.5, 2046.6 and 2035.7 cm⁻¹) than those of Fe(CO)₄(N₂), suggesting oxidation of the metal centre, fig. 4. The same new bands are observed on UV photolysis of Fe(CO)₅ in PE under a pressure of H₂, fig. 5, and they can be assigned to the known dihydride, Fe(CO)₄(N₂) leads to displacement of N₂ by H₂,



Fig. 4. IR spectra illustrating the reaction, in PE film at 210 K, between $H_2(1000 \text{ psi})$ and $Fe(CO)_4(N_2)$, generated from $Fe(CO)_5$ and N_2 . (a) Spectra recorded at the start of the reaction and then at intervals of ≈ 10 min thereafter; in each spectrum the bands of $Fe(CO)_5$ have been removed by computer subtraction to aid visualisation. (b) Unscaled IR difference spectrum (final spectrum *minus* initial spectrum) showing the overall effect of the reaction; bands in the + direction are assigned to $Fe(CO)_4H_2$ and those in the - direction to $Fe(CO)_4(N_2)$. Note that all of these spectra were recorded in the same experiment as those shown in fig. 2.



Fig. 5. IR spectra obtained during the UV irradiation ($\lambda > 300$ nm) of Fe(CO)₅ in PE at 250 K under a pressure of H₂ (400 psi). The uncoloured spectrum was recorded at the start of the experiment and the coloured spectrum, after 25 min UV irradiation. Notice that the principal bands in the coloured spectrum, due to Fe(CO)₄H₂, are identical to those observed in the *thermal* reaction of Fe(CO)₄(N₂) with H₂, fig. 4.

$$\operatorname{Fe}(\operatorname{CO})_4(\operatorname{N}_2) + \operatorname{H}_2 \xrightarrow{\mathrm{UV}} \operatorname{Fe}(\operatorname{CO})_4 \operatorname{H}_2 + \operatorname{N}_2.$$
 (3)

The kinetics of this reaction appear to be complex. When the rate of reaction was monitored with the absorbance of the ν (C-O) band of Fe(CO)₄(N₂) at 1972 cm⁻¹, we did *not* obtain linear plots for either A versus time (zero order) or for ln A versus time (first order). This kinetic behaviour suggests that, under these conditions, the rate of reaction is influenced not only by the thermal stability of Fe(CO)₄(N₂) itself but also by the diffusion of H₂ into the PE film ^{#4}.

4. Discussion

Until now, little has been known of the thermal stability or of the chemistry of $Fe(CO)_4(N_2)$. Although it is still difficult to gauge the precise stabilising effect of the PE matrix, the experiments described here suggest that $Fe(CO)_4(N_2)$ has a thermal stability at least as great as that of the corresponding compound of nickel. Ni(CO)₃(N₂) reacts rapidly with CO in the present of a large excess of N₂ in liquid Kr solution at 165 K [22] (i.e. over 50 K lower than the temperature at which $Fe(CO)_4(N_2)$ reacts with H_2 in PE). On the other hand, $Fe(CO)_4(N_2)$ appears to be considerably more reactive than $Cr(CO)_{5}(N_{2})$ which has a lifetime of ≈ 1 s in fluid solution at room temperature under 1 atm pressure of N_2 [23]. The reaction of $Fe(CO)_4(N_2)$ with H_2 is interesting because it implies that the dihydride, $Fe(CO)_4H_2$, has greater thermal stability than the dinitrogen complex, $Fe(CO)_4(N_2)$. This contrasts sharply with a range of non-classical dihydrogen complexes where the corresponding dinitrogen complex is more stable and η^2 -H₂ can easily be displaced thermally by N2, see, e.g., ref. [24]. It is unlikely that this difference in behaviour is merely the result of the formal oxidation of the metal centre on addition of hydrogen, because in some dihydrogen complexes, e.g. $(C_5H_5)Nb(CO)_3(\eta^2-H_2)$ [25], where H₂ can be displaced by N₂, the energy difference between dihydrogen and dihydride complex is very small, $\leq 4 \text{ kJ mol}^{-1}$. Our experiments have also provided a strong indication that the structure of $Fe(CO)_4(N_2)$ involves an equatorial N₂ group.

These reactions have been studied at temperatures, close to the glass transition of PE and it has been striking that quite small changes in temperature have had a marked effect on the outcome of the UV photolysis. Below 190 K, much less $Fe(CO)_4(N_2)$ is formed while, at temperatures above 190 K, increasing amounts of polynuclear products are formed. We have recently shown that $(C_5Me_5)Ir(CO)_2$ appears to be immobilised in PE at ≈ 190 K, although it is relatively mobile at higher temperatures [26]. The temperature dependence of the photochemistry of Fe(CO)₅ is presumably the result of the changing mobility of the various species in the PE matrix, an effect which warrants further investigation.

The technical aspects of these experiments have implications, considerably wider than the chemistry of $Fe(CO)_4(N_2)$. The use of our high-pressure cell provides a bridge between conventional solid gas matrices and high-pressure experiments at ambient temperature. It is easy and quick to change the reactant gases, and, for the first time, it is possible to *decrease* the concentration of the organometallic in the matrix once the experiment has started, by in situ supercritical extraction. Successful preliminary results have already been obtained for other transition metal compounds. In principle, the experiments are not limited to reactions with gases alone. Recently,

¹⁴ For a recent discussion of gases in polymers, see ref. [21].

we showed that temperature-dependent H-bonding to metal centres of organometallic compounds can be observed in PE films saturated with liquid fluoroalcohols [26]. We are now exploring the possibility of using our high-pressure cell to investigate reactions, such as hydrogenation or carbonylation, which involve organometallics, gases *and* liquids.

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