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Review Commentary

Intermediates in organometallic and organic chemistry: spectroscopy, polymers, hydrogenation and supercritical fluids

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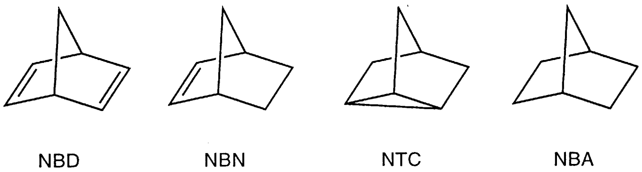
ABSTRACT: IR spectroscopy has transformed the study of mechanistic organometallic chemistry. Reaction intermediates can now be detected and characterized; their kinetics can be measured and their behaviour understood. However, the field is not static. New techniques are still being developed. We focus here on hydrogenation and related reactions describing (i) a miniature low-temperature/high-pressure cell, which allows photochemical reactions to be studied *under high pressures* of gases, (ii) the use of flow reactors for continuous reactions in supercritical fluids, including hydrogenation of organic compounds, and (iii) the use of supercritical fluid solutions for studying weak metal–ligand interactions by nanosecond time-resolved IR spectroscopy (TRIR) and the application of TRIR to the detection of intermediates in organic reactions. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: intermediates; spectroscopy; polymers; hydrogenation; supercritical fluids

EXPERIMENTS AT LOW TEMPERATURE AND HIGH PRESSURE

Matrix isolation has made an enormous impact on the understanding of organometallic intermediates.[1] Traditionally, the technique has involved the generation of organometallic intermediates in noble gas matrices, but this approach suffers from considerable limitations when applied to homogeneously catalysed reactions such as hydrogenation. There are two difficulties: (i) how to trap all of the components of the reaction mixture (substrate, H_2 and catalyst) in close proximity in the matrix and (ii) how to vary the temperature over a sufficiently wide range both to freeze out the reaction intermediates for spectroscopic identification, but also to warm the reaction mixture sufficiently for the reaction to occur within the matrix. Rest and co-workers[2] have shown that the temperature limitation can be avoided by using polyethylene (PE) as a matrix for studying photochemical reactions over the *whole* temperature range 20–300 K. We have developed this idea further, by devising a miniature high-pressure cell[3] which can be pressurised with gases such as H_2 yet still can be cooled to 30K. We illustrate the role of our cell by showing how it can be used to follow the key stages in the hydrogenation of norbornadiene, (NBD) (Scheme 1) from reactants via intermediates to products in a way which would be difficult by any other method.



Scheme 1

The hydrogenation of NBD is catalysed photochemically by the Group 6 metal hexacarbonyl complexes, $M(CO)_6$. This reaction is mechanistically complicated since it can produce three products, NBN, NTC and NBA. The distribution of these products depends on both the metal and the reaction conditions.[4] The mechanism has been studied extensively over the past 25 years, including a very detailed investigation[5] which combined the results of matrix isolation, time-resolved IR spectroscopy (see below) and cryogenic liquid Xe experiments. The overall conclusion is summarized in Scheme 2,

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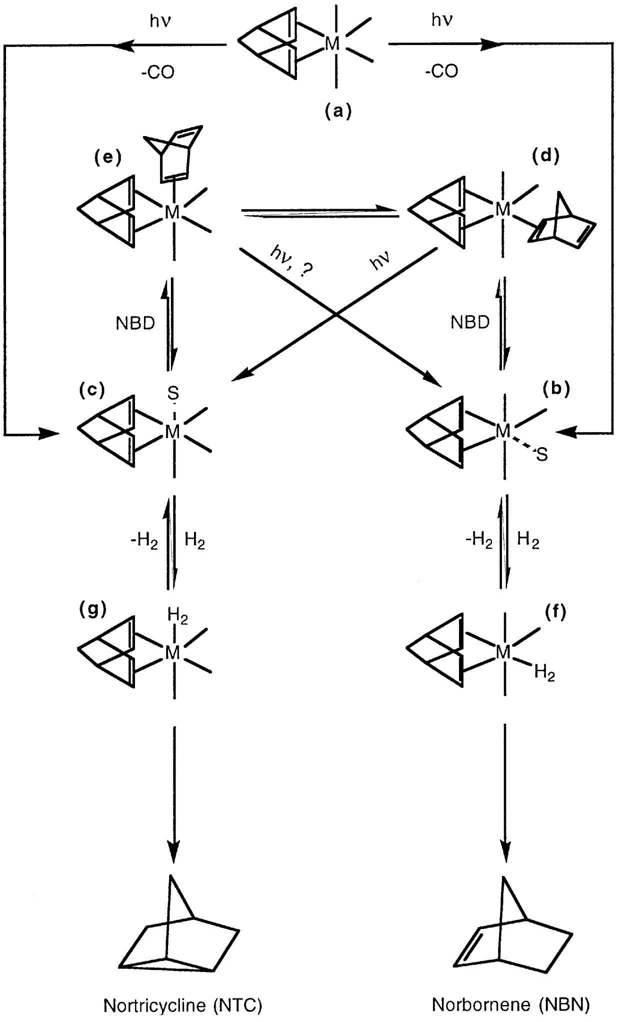


Scheme 2. M = Cr or Mo. The scheme omits the initial formation of (NBD)M(CO)$_4$, **a**, from M(CO)$_6$. The other intermediates in the reaction are labelled **b** to **f**, and these labels are used in the discussion below. S denotes a molecule of solvent, typically hexane (adapted from Ref. 5)

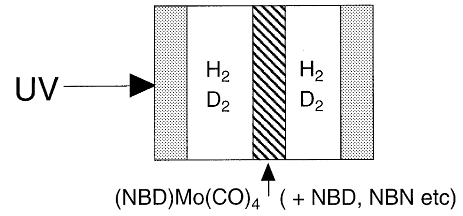


Figure 1. A schematic diagram showing how the low-temperature/high-pressure cell can be used to monitor the hydrogenation (or deuteration) of NBD. The cell contains a disk of PE which, prior to the experiment, is impregnated with the catalyst (NBD)Mo(CO)$_4$ and an organic substrate (NBD, NBN, etc.) as appropriate. The cell is then pressurized with H_2 or D_2 to the required pressure. Hydrogenation can be initiated by UV photolysis through the CaF_2 windows of the cell and the subsequent reaction can be monitored by FTIR spectroscopy through the same windows. Full experimental details are available in Ref. 6

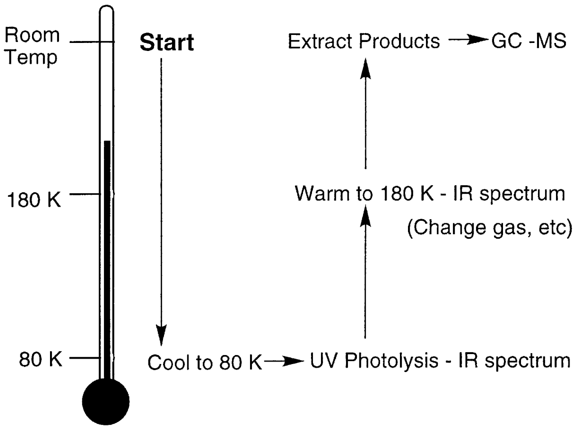


Figure 2. Outline of the different stages of a typical experiment in the low-temperature/high-pressure cell. Before the 'start,' the PE disk is impregnated with (NBD)Mo(CO)$_4$ and the appropriate organic substrate. At the end of the experiment, the reaction products are extracted with CH_2Cl_2. About 1–10 μg of the organometallic are normally impregnated into a PE disk of 250 μm thickness; with these quantities, the extraction provides sufficient material for *ca* 15 replicate analyses of the products. Further details are given in Ref. 6

which provides plausible pathways for the formation of NBN and NTC but not of the fully hydrogenated product NBA.

Figure 1 outlines the way in which the low-temperature/high-pressure cell can be applied to the hydrogenation of NBD and Fig. 2 summarizes the stages of a typical experiment. The advantage over other techniques is that this approach gives the experimenter the freedom (i) to vary the temperature from ambient down to 30 K so that the reaction can be frozen at any stage, (ii) to change gases rapidly and efficiently *during the experiment* and (iii) to recover and analyse the products by GC–MS at the end of the reaction. Figure 3 shows IR spectra obtained from two experiments, performed in the absence and presence of H_2.

Most of our recent experiments have focused on the mechanism of formation of the fully hydrogenated product, NBA. The key to our understanding of this process has been the ability to switch between H_2 and D_2 at any time during the experiments and to analyse the isotopic composition of the NBA by GC–MS with single ion detection (see Fig. 4).

The conclusion from these experiments was that NBA can be formed by *two different routes* depending whether the reaction is stoichiometric [i.e. the reaction of (NBD)Mo(CO)$_4$ and H_2] or catalytic (i.e. when the reaction is carried out in the presence of excess NBD) (Scheme 3). The catalytic mechanism involves a two-stage hydrogenation of NBD. Initially NBD is converted to NBN as shown in Scheme 2, which is released into solution. In the second step, free NBN is hydrogenated to

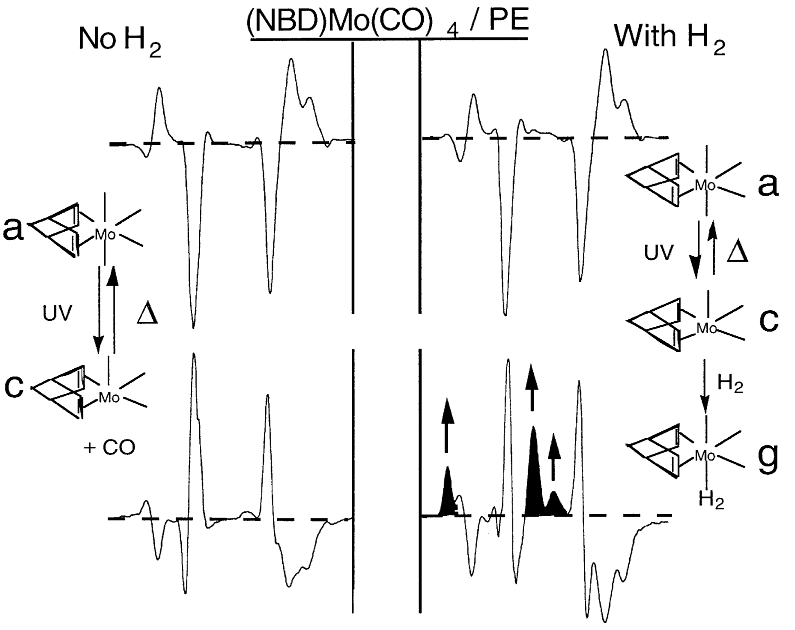


Figure 3. IR spectra illustrating the effects of UV photolysis of (NBD)Mo(CO)$_4$, **a**, in PE at 80 K with H_2 (spectra on the right-hand side) and without H_2 (spectra on the left) and the results of subsequent warming of the PE disk. All spectra are *IR difference spectra* (i.e. spectra generated by subtracting the spectrum recorded before an event from that recorded after). In such spectra, bands due to species which are formed by that event are shown pointing upwards, while bands due to species which are destroyed point downwards. In both experiments, UV photolysis destroys **a** and causes the formation of the coordinatively unsaturated species **c**, whether H_2 is present or not. There is, however, a difference in behaviour on warming. In the absence of H_2, **a** is regenerated directly from **c**. In the presence of H_2, **c** reacts to form the dihydrogen complex, **g**, the bands of which are coloured black. All spectra recorded at 2 cm^{-1} resolution. Spectra are shown in *absorbance*. The strongest positive peak in the both of the upper spectra correspond to an absorbance of *ca* 0.3

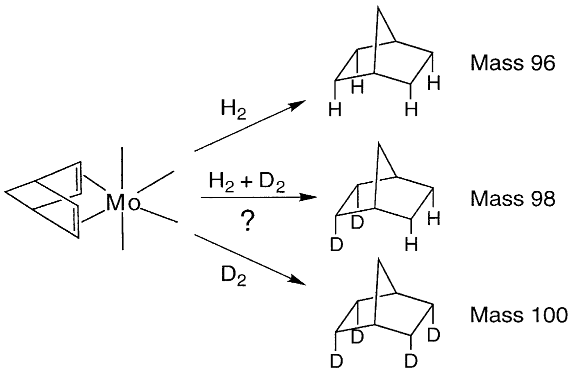
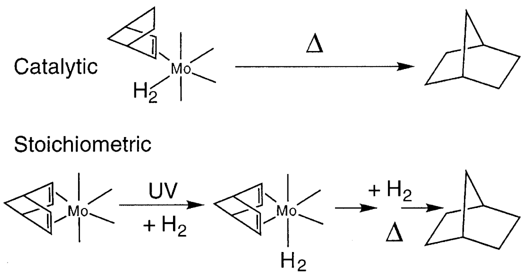


Figure 4. Scheme showing the possible isotopomers of NBA, formed during the hydrogenation or deuteration of NBD. GC–MS (VG Biotech Trio 2000) was used in the single ion mode to quantify the relative amounts of mass 96, 98 and 100 formed when H_2 and D_2 were used in the same experiment. A whole series of such experiments were carried out: H_2 and D_2 were premixed; the gases were used sequentially, H_2 *before* D_2 or H_2 *after* D_2; the gases were used separately but were frequently interchanged (5 min H_2 followed by 5 min D_2), etc. Note that the positions of the H and D labels in NBA are not intended to represent any particular stereochemistry



Scheme 3. Mechanisms proposed for the formation of NBA in both catalytic and stoichiometric hydrogenation of NBD by (NBD)Mo(CO)$_4$

NBA via *cis*-(η^2-NBN)Mo(CO)$_4$(H_2). The stoichiometric hydrogenation of NBN proceeds by a different mechanism which we have only been able to document partially; it involves the formation of *fac*-(η^4-NBD)Mo(CO)$_3$(H_2) followed by more than one thermal step, with intermediates sufficiently long-lived in PE to undergo at least partial exchange of the coordinated H_2 for D_2.

Hence, as in all mechanistic studies, there are opportunities for further investigation. Nevertheless, these experiments have provided the first definite mechanisms for the formation of NBA, the production of which has previously be regarded as a side-reaction. The reason why we have been able to obtain this extra information is that the use of PE matrices in the low-temperature/high-pressure cell has allowed us to manipulate the reaction much more precisely than has previously been possible.

Increased control of reactions is also provided by supercritical fluids which form the second part of this paper.

REACTIONS IN SUPERCRITICAL FLUID SOLUTION

Supercritical fluids are gases compressed until their densities approach those of liquids. If the temperature of the fluid is close to its critical value, T_c, the fluid displays an intriguing mixture of the properties of a gas and a liquid.[7] In particular, the fluid can be used as a solvent for chemical reactions, often with distinct chemical and environmental advantages over more conventional solvents.[8] There are a surprising number of materials with T_c close to ambient. Here we describe the use of only three (Xe, 16.8 °C; CO_2, 31.6 °C; and propane, 96.8 °C).

Gaseous H_2 has relatively low solubility in conventional organic solvents, placing significant limitations on reactions such as hydrogenation, which involve addition of H_2 to substrates. By contrast, H_2 is *completely miscible* with supercritical (sc) fluids such as scXe, $scCO_2$ or sc-propane. Our research group was one of the first to exploit this miscibility to synthesize highly labile organometallic dihydrogen compounds[9] of metals in Groups 6, 7 and 8. This enhanced concentration of H_2 has since been exploited to accelerate hydrogenation of organic substrates and even of $scCO_2$ itself.[10]

Dihydrogen complexes contain the η^2-H_2 group coordinated to a metal centre. First characterized by Kubas *et al.*,[11] these compounds have now been found to be fairly widespread. Indeed, unstable dihydrogen complexes are key intermediates in the hydrogenation of NBD (see above). In our supercritical experiments, the dihydrogen compounds were generated photochemically by the direct reaction of H_2 with a transition metal carbonyl complex.[9] Several of these compounds had not been observed previously and, surprisingly, some of them [e.g. $CpMn(CO)_2(H_2)$, $Cp = \eta^5$-C_5H_5] appeared to be extremely stable, even though they lacked the bulky phosphines which were thought to be necessary to stabilize such complexes. Initially, the compounds had been made in a small spectroscopic cell (total volume >1.5 ml) but their stability suggested that they might be isolable. The problem was how to isolate them from the supercritical solution because uncontrolled release of the pressure would result in the compound being deposited as a highly dispersed powder over the entire inside surfaces of the apparatus. The solution was to conduct the reactions in a continuous flow reactor. Figure 5 shows the miniature flow system which we devised[12] for scaling up the preparation of $CpMn(CO)_2(H_2)$. Once isolated, $CpMn(CO)_2(H_2)$ was found to be a low melting point yellow solid (the starting material is nearly white) with a surprisingly low airsensitivity.

We have now extended this flow reactor concept to hydrogenation. We have built a reactor which can be used for continuous catalytic hydrogenation of a wide range of organic compounds with high efficiency. Three groups have previously published work in this area. Pickel and Steiner[13] used a continuous supercritical hydrogenator for unspecified reactions of pharmaceutical interest, while Tacke *et al.*[14] and Härröd and co-workers[15] concentrated on the hydrogenation of fats, relevant to the food industry. Our reactor, shown in Fig. 6, differs from this earlier work in that it is designed to operate with a very wide range of organic substrates and functionalities.

The reactor was initially tested with the hydrogenation of cyclohexene (Scheme 4). This reaction revealed several advantages of hydrogenation under supercritical fluid conditions: the reaction is not limited by mass transfer effects; the fluid has good thermal properties; and, on a small scale at least, reactions can be carried out with good selectivity and very high space time yields.[16] Thus, we have found that cyclohexene could be hydrogenated at a rate of 20 ml min^{-1} using only 4 ml of

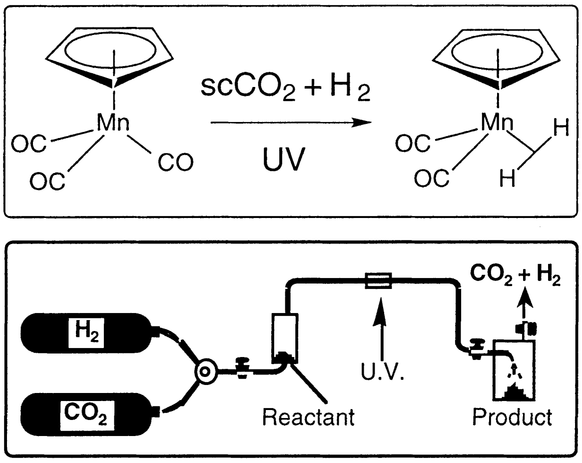


Figure 5. Schematic view of a continuous flow reactor for the synthesis and isolation of $CpMn(CO)_2(H_2)$, labelled 'Product,' from $CpMn(CO)_3$, labelled 'Reactant.' The overall reaction is very simple, as shown at the top, and is typically carried out a total pressure of 3000 psi (20 MPa). Initially H_2 and CO_2 are mixed. The solid reactant $CpMn(CO)_3$ is then dissolved in the supercritical H_2–CO_2 mixture and is flowed past a UV lamp which converts reactant to product. FTIR monitoring, not shown, is used to adjust the reaction conditions (pressure, temperature, flow-rate, etc.) for optimum conversion. The product, $CpMn(CO)_2(H_2)$, is then isolated from solution by rapid expansion through a back-pressure regulating valve. It is this rapid expansion which is the key to the success of this synthetic route. Labile ligands, such as η^2-H_2, are easily lost when compounds containing them are subjected to the vacuum used for the removal of conventional solvents. In the supercritical flow reactor, the compound is maintained under a high pressure of H_2 right up to the moment that precipitation of the solid product begins. Full experimental details are given in Ref. 12. **Safety note:** *Supercritical fluid experiments involve high pressures and should only be carried out in apparatus with the appropriate pressure ratings and safety precautions*

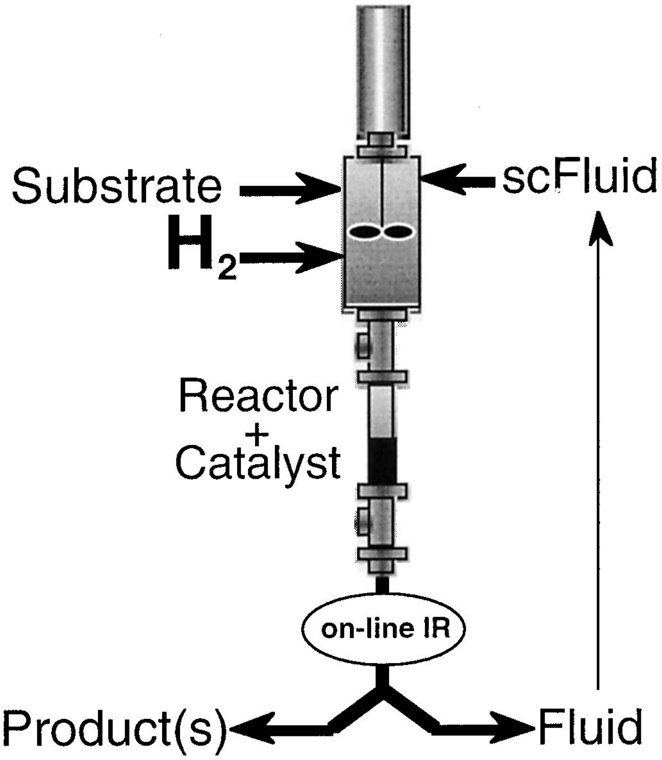
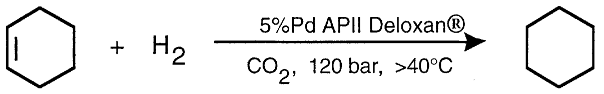


Figure 6. Block diagram of the key components of our flow reactor for continuous hydrogenation of organic compounds. $scCO_2$, H_2 and the organic substrate are mixed in a heated mixer. The mixture is then passed through a reactor containing a fixed-bed catalyst (usually a supported noble metal). There is the option of on-line FTIR monitoring before the product and CO_2 are separated by expansion as in Fig. 5. The equipment is based on modules from NWA (Lörrach, Germany). Although the volume of the reactor is very small (only 5 or 10 ml), the equipment can generate up to 1200 ml of product per hour in favourable reactions



Scheme 4. Reaction carried out in the flow reactor, illustrated in Fig. 6. Deloxan is an aminopolysiloxane catalyst support made by Degussa

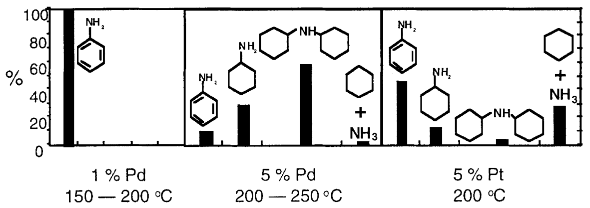
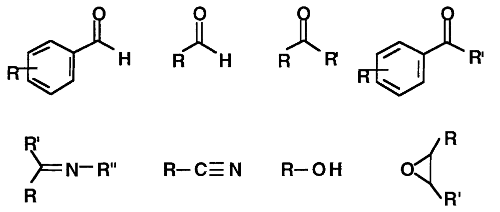


Figure 7. Summary of the product distribution obtained in the hydrogenation of nitrobenzene in sc-propane over a series of different metal catalysts, all supported on Deloxan. Flow-rates were *ca* 0.5 ml per min^{-1} of organic, which corresponds to a residence time of <5 min in the reactor. Note that the efficiency of the reactor is sufficiently high for 25% of the substrate to be fully hydrogenated to NH_3 and C_6H_{12}



Scheme 5. Some of the other functional groups which have been successfully hydrogenated in our reactor. In each case, the hydrogenation proceeds with a high degree of conversion (usually $>90\%$) and with a high degree of selectivity. Where more than one product is possible (e.g. a ketone being reduced to alcohol or alkane), the conditions can often be optimized to give a high yield of the desired product. Full details are given in Ref. 28

catalyst with no apparent loss of performance over a period of hours. Experiments confirmed that comparable results can also be achieved with isophorone, a commercially significant derivative of cyclohexene. In this case, supercritical hydrogenation appears to be more selective and to use less catalyst than existing processes in gas or liquid phase.

Figure 7, and Scheme 5 illustrate the wide range of other functionalities which can be hydrogenated under supercritical conditions, either in $scCO_2$ or sc-propane. We have found that supercritical fluids provide a very high degree of control over the hydrogenation. A wide variety of reaction parameters (temperature, pressure, ratio of H_2 to substrate, etc.) can be varied almost *independently*. Overall, therefore, supercritical fluids allow H_2 to be used as a reagent far more easily than in current practice. Although the scale is already larger than might be required in many academic experiments, the entire reactor can be accommodated in half a standard fume-hood. On the other hand, relatively modest scale-up would be required for commercial production of fine chemicals.

TIME-RESOLVED IR SPECTROSCOPY

In the previous section we described the use of $scCO_2$ for heterogeneous hydrogenation. The fluid has also attracted considerable attention for homogeneous hydrogenation. Several groups have found increased rates or increased selectivity in $ScCO_2$ compared to homogeneous reactions in conventional solvents.[10,17] Much of this improvement has been derived from the increased concentration of H_2. Time-resolved IR spectroscopy (TRIR), a combination of UV flash photolysis with fast IR detection, is now allowing us to quantify the effect of this increased concentration on the rates of the primary steps in such

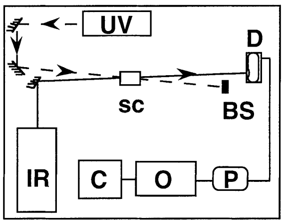


Figure 8. Layout of the Nottingham TRIR spectrometer. UV = Nd:YAG laser; IR = IR diode laser; SC = supercritical cell; D = MCT IR detector; P = preamplifier; O = digital storage oscilloscope; C = computer and BS = beam stop. Adapted from Ref. 18b

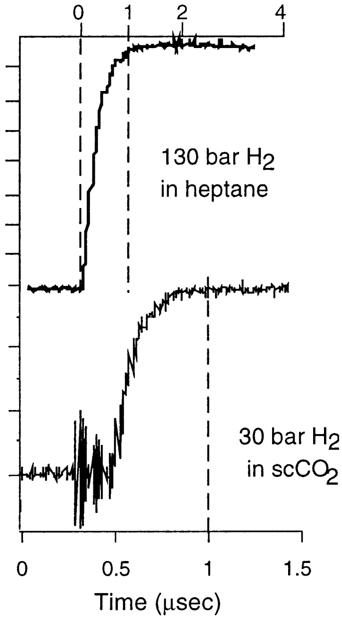


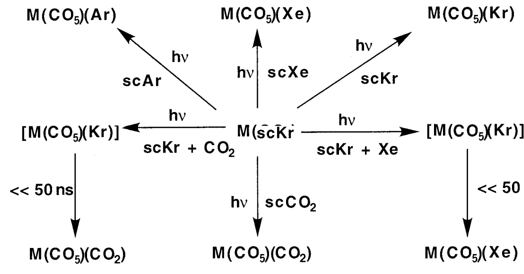
Figure 9. TRIR traces comparing the rates of formation of $Cr(CO)_5(H_2)$ in *n*-heptane and $scCO_2$ solution. Note the different scales on the abscissa (time axis) for the two traces (adapted from Ref. 18b)

reactions.[18] TRIR is especially suited to the study of organometallic reactions, particularly those involving metal carbonyl compounds.[18a] Our current apparatus consists of an IR diode laser which is tuned to a particular IR frequency and is used to monitor changes in IR absorption of a reaction solution following a UV laser pulse. The IR laser is then retuned to another frequency and the process is repeated. Thus IR spectra are built up *point-by-point* by plotting change in absorbance versus wavenumber (see Fig. 8). The relatively narrow linewidths of v(CO) absorptions make it possible to monitor several key species in solution at the same time; destruction of reactants and formation of excited states, intermediates and products can all be followed.

We applied TRIR to the reaction of $Cr(CO)_6$ with H_2 in order to investigate the effects of increased H_2 concentrations in $scCO_2$. This reaction[5,19] generates the dihydrogen complex, $Cr(CO)_5(H_2)$. Figure 9 compares the rates of formation of $Cr(CO)_5(H_2)$ in *n*-heptane and in $scCO_2$ by monitoring the reaction at the wavenumber of the *e* ν(CO) absorption band of $Cr(CO)_5(H_2)$. Allowing for the different pressures of H_2, the rate in $scCO_2$ is *ca* 16 times faster than in *n*-heptane. However, one cannot equate this difference in rate directly with the difference in effective concentration of H_2 within the medium. The $Cr(CO)_5$ intermediate, which is formed in the reaction, is not 'naked' because a solvent molecule, s, occupies the otherwise vacant coordination site as a so-called 'token' ligand:[19]

$$Cr(CO)_6 \xrightarrow{UV} Cr(CO)_5 \xrightarrow{+s} Cr(CO)_5s \xrightarrow{+H_2} Cr(CO)_5(H_2)$$

Thus the rate of reaction of $Cr(CO)_5s$ with H_2 depends not only on the concentration of H_2 but also on the strength of the Cr–s interaction. By using TRIR to follow the reactions of the W analogue[21] $W(CO)_5s$ in the absence of H_2, we have shown that the interaction with CO_2 has approximately half the strength of that with *n*-heptane. Furthermore, our TRIR study produced the first, albeit tentative, evidence for η^1-O coordination of CO_2 close to room temperature.[21] TRIR allowed us to characterize $M(CO)_5(CO_2)$ (M = Cr, Mo and W) following photolysis of $M(CO)_6$ in $scCO_2$, which is a unique solvent for studying CO_2 coordination as it offers the highest possible concentration of CO_2. Although the metal ν(CO) IR vibrations are easily observed, the parts of the IR region where we expect to see the key bands of coordinated CO_2 are masked by the absorptions of CO_2 solvent. We have used other supercritical fluids, such as Xe and Kr, which are non-absorbing, to overcome this problem; work is still in progress to improve the sensitivity of our TRIR equipment in these newly unmasked regions of the spectrum. Using the rate constants for reaction of $M(CO)_5s$ with CO as a crude measure of reactivity, we found that the $M(CO)_5(OCO)$ had very similar reactivity to the corresponding Xe complexes $M(CO)_5(Xe)$ generated by photolysis of $M(CO)_6$ in supercritical Xe (scXe) (Scheme 6).

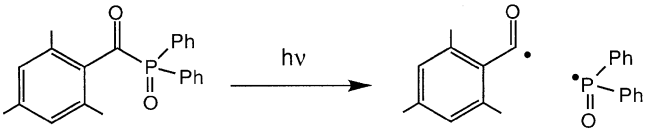


Scheme 6

TRIR AND ORGANIC INTERMEDIATES

The difficulty in applying TRIR to organic photochemistry has been that IR bands usually have much lower extinction coefficients than UV–visible bands so that there have been relatively few applications of TRIR to organic photochemistry. Some years ago, work at Nottingham demonstrated that didehydroazepine, formed following irradiation of phenyl azide in solution, can be characterized by TRIR and its subsequent reaction with diethylamine can be monitored.[22] In collaboration with Tomioka and co-workers, we have recently used TRIR to elucidate the photochemistry of 2-(methoxycarbonyl)-phenyl azide in heptane solution.[23]

Vibrational spectroscopy is a very powerful probe for studying the nature and the structure of organic excited states. The spectrum of the $\pi\pi^*$ triplet excited state of 4-phenylbenzophenone showed that both the frequency and intensity of the ν(CO) bands are a highly sensitive diagnostic of the $\pi\pi^*$ state.[24] Lusztyk and co-workers used TRIR to probe the kinetics of cumyloxyl radicals produced following flash photolysis of diamyl peroxide in CCl_4 solution[25] and they have extended this work to elucidate the reactivity of a range of acyl radicals.[26] We have used this approach in collaboration with Turro and co-workers to study the photoinitiator (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (Scheme 7), and to show that its reaction kinetics can easily be measured.[27]



Scheme 7

CONCLUSIONS

This paper has outlined several new developments in the detection of reaction intermediates and in related areas of chemistry. All of these developments, polymer matrices, supercritical fluids and time-resolved IR are still evolving and we expect significant advances in the near future. In the polymer matrices, we believe that the use of polymers other than polyethylene will broaden the range of chemistry which can be studied, particularly to more polar organometallic compounds. In supercritical fluids, the concept of continuous fixed-bed catalytic reactors will undoubtedly be applied to further organic reactions, improving both their selectivity and reducing their environmental impact. In TRIR, new spectroscopic techniques, particularly *step-scan Fourier transform IR*, are likely to widen the spectral region accessible to TRIR. This will enable TRIR to be used much more widely as a probe in mechanistic organic chemistry.

Acknowledgements

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