PHOTOCHEMISTRY OF SOME METAL CARBONYLS IN FROZEN SOLVENT GLASSES

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Summary

Photolysis reactions of $Fe(CO)_5$, group VI hexacarbonyls, some substituted group VI hexacarbonyl derivatives, and cyclopentadienyl manganese tricarbonyl and some related compounds in hydrocarbon glass have been examined. Reactions in the more reactive glass, 2-methyltetrahydrofuran, and reactions of the above species in hydrocarbon glass in the presence of some potential ligands have also been examined. The glass temperature throughout this work was 77K.

Reaction monitoring throughout was by i.r. spectroscopy, mostly observing the carbonyl stretching region only, and the object of the work was to observe the results of photolysis in glasses and to correlate these with results obtained in very low temperature gas matrices and in solution by other workers rather than to determine the actual photolysis mechanisms. In many experiments glasses containing photolysis fragments were deliberately allowed to warm up beyond the glass softening temperature and the changes occurring on glass softening were monitored in an attempt to link the results obtained in the glasses with results of photolysis in solution where molecules are free to associate.

The predominant reaction in all the systems studied in glasses was stepwise CO loss, and many CO deficient fragments have been observed and identified as far as is possible from their i.r. spectra. In cases where the results of matrix

isolation studies were available the results obtained in this work are consistent with these. The results obtained in hydrocarbon glass also support the view that saturated hydrocarbon interacts with CO deficient metal carbonyl fragments to an extent not realised until very recently. Another point of general interest which has arisen from the photolysis reactions in hydrocarbon in the presence of added donors is the importance of pre-photolytic association of carbonyl and potential ligand. The possible effect of this type of association on solution photochemical reactions does not seem to have been previously recognised and should certainly be investigated.

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Introduction

Stable metal carbonyls have been known since the turn of the century[1] and the mechanisms of their thermolysis and photolysis have been of interest for at least the last fifteen years.[2,3] The principal reason for this interest has almost certainly been the potential catalytic importance of metal carbonyls. Before 1960 most of the work done on metal carbonyls was concerned with their reactions with bases[4] and oxidising[5] and reducing[6] agents in polar solvents, the main interest being the unusual oxidation states of metals obtainable in these reactions e.g. $Fe^{(-2)}$ [6]. However, in the course of this work many neutral derivatives of the stable carbonyls were discovered and it was found that metal carbonyl derivatives could be prepared including a great variety of basic (σ donor) ligands.[7] Following the development of metal cyclopentadienyl chemistry in the 1950's, a large number of metal carbonyl derivatives including π donors such as cyclopentadiene were made around 1960.[8,9] As in most of these derivatives the coordinated ligand was activated in some way relative to free ligand, yet most of the ligand additions were reversible, it was realised that unsaturated metal carbonyl fragments could have catalytic properties or function as reaction initiators. Since then many catalytic processes involving metal carbonyls have been studied.[10,11]

Interest in the nature of unsaturated carbonyl fragments, which was also stimulated by theoretical questions about molecular geometry[12] and the nature of metal-carbon bond cleavage,[13] coincided with the advance of i.r. spectroscopy, which proved a particularly useful technique for their study, in the 1960's. The first isolation and structure determination of an unsaturated metal carbonyl fragment was accomplished by Stolz, Dobson, and Sheline in 1963.[14]

During the 1960's many kinetic studies of metal carbonyl substitution reactions were made[15,16] and it was shown that an important mechanism in all the photochemical and most thermal reactions of unsubstituted carbonyls was loss of one CO group followed by substitution with another ligand. The availability of matrix isolation techniques around 1970 allowed much more detailed study of unsaturated carbonyl fragments,[17,18] but under conditions very different from those normally existing in reaction systems.

In this work the photochemistry of unsubstituted and substituted group VI carbonyls, pentacarbonyl iron, and cyclopentadienyl manganese tricarbonyl has been studied in frozen solvent glasses, using a similar technique to that of Stolz,Dobson, and Sheline, to try to show what the solution photolysis intermediates actually are, and to provide a link between matrix isolation and solution photolysis work.

The actual nature of the excitation processes and the excited states involved were not investigated. It is interesting to note that all the primary photochemical reactions observed involve loss of a two electron donor ligand (usually CO) whereas in organic photochemistry the predominant primary process is homolytic fission of a single covalent bond to give radicals. A molecular orbital energy level diagram has been constructed for $Cr(CO)_6$.[19] In the $Cr(CO)_6$ case the most likely excitation to give rise to CO dissociation (at least with the energy of light used) is the $2t_{2g} \longrightarrow 4t_{1u}$ transition (ν 35700 cm^{-1}). This is mainly a charge transfer transition from metal to CO and may be followed by intersystem crossing to a triplet state before[20] dissociation of CO. Photolysis of $Mo(CO)_6$ and $W(CO)_6$ probably proceeds by a similar mechanism. In the case of substituted hexacarbonyls no quantitative energy level diagrams are available, but it has been suggested that the lowest energy metal to CO charge transfer is to the four CO ligands in the equatorial plane.[21] The relative energies of the metal to CO and metal to ligand transitions are, however, unknown. Again only a qualitative energy level diagram is available for $Fe(CO)_5$[22] and even less about the electronic mechanism of photolysis is known in that case.

Matrix Photolysis

Photolysis reactions in a solid phase such as a frozen glass or a solid argon matrix are not only dependent on electronic factors but also on the physical interactions of the starting material and reaction products with the matrix. An isolated molecule can be thought of as being in a cage formed by the matrix molecules around it, and, if the molecule is photolysed, the fragments must be produced with sufficient kinetic energy to escape from the matrix cage. This can mean that the matrix photolytic reactions of a species are different from the primary reactions of the same species in gas phase or solution.[23,24] Normally only very light fragments (e.g. CO) will be lost in matrix photolysis while in gas phase and solution photolysis there is evidence for loss of trialkyl phosphines from $W(CO)_4(P(C_3H_7)_3)_2$ for example.[24]

Another phenomenon evident in photolysis in rigid media which may not occur in gas phase or solution is 'photoreversal' in which the initial photolysis is reversed on irradiation with lower energy light. Of course the importance of such a process in non-rigid media is impossible to asses since there is bound to be a large amount of recombination of photolytic fragments by thermal pathways, in organometallic systems at least. Until very recently it was thought that photoreversal in inert glasses and matrices was in fact a thermal process[25,26] proceeding in two steps. First lower energy light was absorbed by an unsaturated fragment and then this fragment lost energy by a radiationless pathway and in so doing caused local softening of the matrix to allow thermal recombination with the other part of the photolysed molecule. However, very recently it has been suggested by Burdett[27] that the time taken for an electronically excited fragment to lose its energy as kinetic energy to all the molecules in the surrounding matrix is very short indeed and that the surrounding matrix would only be non-rigid for the same order of time as the period of a molecular vibration. This seems to be in agreement with the fact that only loss of very light fragments has been observed in matrix photolysis where it appears that, if efficient photolysis takes place, the excess energy of the photolytic fragments is transferred mainly to the lighter fragment in the form of kinetic energy,rather than being transferred to all the molecules in the surrounding matrix. Other evidence which could be taken as support for Burdett's view on local matrix softening is the observation of the high energy conformers of $Fe(CO)_3(MTHF)_2$ and $CpMn(CO)_2(MTHF)$ in hydrocarbon glass, which will be discussed in detail in later chapters. If local matrix softening takes place on absorption of low energy light, the above species would be expected to rearrange to predominantly their minimum energy conformation on prolonged irradiation.

This was not observed. In the cases where rearrangement was observed (i.e. LMo$(CO)_4$ etc.) the preferred conformer depended on the wavelength of the irradiating light and so the isomerisation must be photochemical rather than thermal. It should be noted, however, that rearrangement of fragments immediately after photolysis is possible and probably occurs in the case of $Cr(CO)_5$ etc. It may be the case that photoreversal is a truly electronic process, but this is by no means well established as yet.

It is important in any study such as this where a highly specialised technique is being used to relate results obtained to observations made in the main stream of preparative chemistry. In the two preceeding paragraphs two important differences between matrix and solution photolysis have been described. However, another important point to bear in mind is that the fragments observed may be radically different from the intermediates involved in solution photochemistry because of the very different reaction conditions (e.g. temperature) used. For example in all cases examined where a metal carbonyl was photolysed in presence of a potential ligand pre-photolytic association of carbonyl and ligand was very important. This could also be the case in room temperature solution reactions, but it is likely that the degree of association is considerably less there. By allowing a glass or other matrix to soften thermally it can be seen whether an unsaturated fragment generated photochemically in that matrix is in its most stable form at the temperature of the soft matrix. However, this does not necessarily give much information about the room temperature stability of that fragment. For example it has been pointed out that $Cr(CO)_5$ generated in an Ar matrix reacts very slowly with CO at about 35K[28], but $Cr(CO)_5$ in hydrocarbon solution at 195K seems to react faster with many non π-acceptor ligands than with CO (as will be discussed in a later chapter), and so it is not surprising that the reaction at 35K with CO is slow although the $Cr(CO)_5$+CO reaction at room temperature is very fast.[89]

It may also be the case that unsaturated fragments interact with a matrix material which is normally thought of as inert and in this way their properties may be considerably modified. The best documented example of this is $Fe(CO)_4$ for which species $Fe(CO)_4Xe$, $Fe(CO)_4Kr$, and $Fe(CO)_4(CH_4)$ have been identified and which probably exists in hydrocarbon at 77K as predominantly $Fe(CO)_4$(alkane), these compounds all being considerably different in structure from $Fe(CO)_4$ in an argon or SF_6 matrix.[29] The group VI pentacarbonyls almost certainly interact with all these materials and this interaction is reflected in shifts in the visible spectrum of $Cr(CO)_5$ between different matrix media.[90] In mixed

Ar:CO matrices both $Cr(CO)_5[CO]$ and $Cr(CO)_5[Ar]$ species can be picked out in the visible spectrum,[30] and similar effects have been observed for group VI pentacarbonyls in other mixed matrices.[90] However, since these species all have very similar i.r. spectra, they are similar in structure and almost certainly in chemical properties. Again this type of interaction has been studied only in matrices at low temperature and its relevance to room temperature solution photochemistry is unknown.

Matrix photolysis at very low temperatures (around 20K) is certainly the best technique available for the production and identification of unsaturated metal carbonyls and the information so obtained has provided much of theoretical interest. Glass photolysis at 77K, on the other hand, provides some sort of link between matrix work and room temperature photochemistry. Glasses can be chosen which have similar properties to solvents in common use. However, there is always a 190 degree temperature difference between the glass and room temperature which may affect reaction rates drastically and three types of processes which commonly occur in solution reactions, i.e. precipitation, gas evolution, and polymerisation cannot occur in the glass.

A common problem in all matrix isolation studies is being certain that the molecules under examination are actually isolated. This can be **difficult** in the case of small gas molecules e.g. for CO in Ar to

Ref, achieve complete isolation of the CO molecules a ratio Ar:CO of 8000:1 was required. Normally starting solutions used in this work were around 10^{-2}M and the solvents were around 7M i.e. a molecule to molecule ratio for glass:solute of 700:1. Although the resolution obtainable in i.r. spectra of glasses was not good enough to show if molecules of starting material were isolated, no evidence for polymeric species in the glass was found, except in cases where crystallisation of some of the starting material was observed, after photolysis. Many of the results were very similar to those observed in inert gas matrices for corresponding molecules. It seems likely, therefore, that isolation is achieved fairly well in most cases by freezing solutions about 10^{-2}M in metal carbonyl, and any polymeric species formed will be very minor products. The ratio of carbon atoms in the glass to starting material, which is probably more comparable with the matrix:solute ratios normally quoted for monatomic and diatomic gas matrices than a molecule:molecule ratio, is around 4200:1. At this dilution a $W(CO)_6$ molecule should be surrounded by eight nearest neighbour glass molecules assuming complete random packing in the glass. It was found that freezing a 10^{-2}M solution of $Fe(CO)_5$ in a 1M solution of a potential ligand in hydrocarbon gave almost 100% association of $Fe(CO)_5$ and ligand (ligand:solvent ratio ~1:7).

The degree to which pre-photolytic association of a stable metal carbonyl with a potential ligand took place was surprising. In the system most closely studied, $Fe(CO)_5$/THF, it was shown that such association would take place in liquid solvent at 120K as well as in frozen glass. Such association had only been noted previously for the $Fe(CO)_5/X_2$/heptane system at 195K (X=Br,I),[31] but it was found to be a general phenomenon for all ligands investigated. The effects of association are more obvious in the i.r. spectrum of $Fe(CO)_5$, but the same type of process occurs with group VI hexacarbonyls and cyclopentadienyl manganese tricarbonyl.

Infrared Spectroscopy

The main method used for observation of isolated species and reaction monitoring throughout this work was infrared spectroscopy looking at only the CO stretching region (2200-1700 cm^{-1}). Since CO stretches in metal carbonyls cause very strong, sharp i.r. absorptions, this technique provides a fairly sensitive and informative method for observation of such species. Also the 2200-1700 cm^{-1} region was free of intense solvent absorptions for all solvents used. The lower limit of concentration required for detection of most metal carbonyls in glass at 77K by observation of their strongest bands was $\sim 10^{-4}$M using 0.1 mm path length. In other regions of the spectrum absorptions are much less intense, and so higher concentrations would be required. Many force constant studies[29,32,33] have shown meaningful information can be obtained by treating the CO stretching frequencies in isolation and a modified CO-factored force field similar to that introduced by Cotton and Kraihanzel[32] is used throughout this work. However, in most cases insufficient frequencies were observed to allow calculations to be made. In gas matrix isolation the problem of lack of observable frequencies is usually overcome by isotopic substitution [25,29], but, since this is more difficult in glass studies (see below), no such experiments were carried out. In a few cases bond angle calculations from i.r. band intensities were possible, but the reliability of such calculations is questionable.[34]

The resolution observed in spectra of glasses was much better than that in the spectra of solutions at room temperature on the same instruments, but was much worse than that observed in most gas matrix isolation studies. Temperature is presumably the most important factor here, but also glass matrix materials all absorb to some extent in the region examined making the use of a reference cell necessary, and attenuation of the reference beam by the reference cell reduced the resolution. The comparatively low resolution (by matrix standards) led to problems in identifying overlapping bands and would have rendered useless any attempt at isotopic substitution experiments. Matrix splittings of bands, common in gas matrices, were not observed, probably because of the lower resolution, and the band shapes were usually quite regular (except in cases where there was association with a potential ligand) after freezing, indicating no strong preference for a particular type of site in the glass, which probably means that all sites are chemically identical. Except where there is association of carbonyl and a Lewis base, cooling has little effect on the CO stretching frequencies.

The Nature of Photolysis Products

Since CO is one of the best π acceptor ligands known, it causes large ligand field splittings and so stable metal carbonyls tend to be eighteen electron species, particularly in the middle of the transition metal series. In the photolysis processes studied the dominant primary reaction is loss of CO and this gives a sixteen electron fragment with more electron density in the M.O.s derived from d_π atomic orbitals than the corresponding eighteen electron complex. Many such fragments are known in matrices[17,18,25,29]. All seem to be thermally stable at least at matrix temperatures, but are extremely reactive towards two electron donors and in some cases even show weak interaction with matrix materials not normally thought of as donors as has been mentioned earlier. Reaction at low temperature with weak σ donors e.g. CO and S_8 to form strongly bonded complexes $M(CO)_{n-1}L$ seems to be considerably slower, but complexes such as $Ni(CO)_3(N_2)$ can still be formed in a matrix at 20K.[36] This last reaction is an example of a sixteen electron fragment reacting with a strongly interacting matrix material, in this case N_2. Another reaction pathway sometimes followed by sixteen electron fragments is polymerisation, possibly via reaction with unphotolysed starting material e.g. $Fe(CO)_4 + Fe(CO)_5 \longrightarrow Fe_2(CO)_9$, where $Fe(CO)_5$ may be functioning as a two electron donor in the initial stages of the reaction. It has also been shown that polymeric species can be formed from group VI carbonyls by photolysis in concentrated gas matrices,[37] but these are presumably species like $M_2(CO)_{11}$ which are likely to be unstable for steric reasons.

The question of whether sixteen electron primary photolytic fragments are generated in their most stable form by photolysis in matrices has been a subject of controversy. Originally Stolz, Dobson, and Sheline[14] in their work on group VI pentacarbonyls suggested that the C_{4v} (square pyramidal) form observed after photolysis in hydrocarbon glass was not the most stable geometry and that new bands occurring on glass softening were due to a more stable D_{3h}(trigonal bipyramidal) isomer. It has since been shown that these bands are due to polymeric species [26,38] and that the C_{4v} form is almost certainly the most stable. A D_{3h} form of $M(CO)_5$ (M=Cr,Mo,W) could well be the initial product of photolysis of group VI hexacarbonyls if the photolysis proceeds via a triplet state[20], but singlet trigonal $M(CO)_5$ would have a degenerate ground state and so would almost certainly undergo Jahn-Teller distortion — probably to a C_{4v} form. $Fe(CO)_4$ would also have a degenerate ground state if it were tetrahedral as had been suggested[12] and the C_{2v} structure observed for $Fe(CO)_4$[29] in matrices could be considered as highly distorted tetrahedral.

Secondary photolysis in inert matrices normally involves loss of a second CO to give a fourteen electron molecule. This is not necessarily more reactive than its sixteen electron precursor. For example $Fe(CO)_3$ does not appear to react with matrix materials in the way that $Fe(CO)_4$ does.[39] Further photolysis leads to loss of yet more CO groups, though in hydrocarbon glass species containing less than three carbonyl groups were very rarely observed. However, in inert gas matrices $Fe(CO)_5$ can be completely photolysed to give iron atoms[39] and in methane at 20K species thought to be $Mo(CO)_2$ and $Mo(CO)$ have been observed.[30]

Rates of photolysis are of course mainly dependent on the u.v. absorption properties of the starting materials, and irradiation conditions were varied to obtain the desired products. For example $Mo(CO)_6$ could be almost completely photolysed in hydrocarbon glass to give $Mo(CO)_5$+CO using light >305 nm, but when higher energy light was used a mixture of $Mo(CO)_5$, $Mo(CO)_4$, and $Mo(CO)_3$ was produced. 305 nm is considerably longer than the wavelength of the absorption maximum of the lowest energy charge transfer band of $Mo(CO)_6$ (280 nm) and photolysis using this lower energy light will be inefficient. However, photolysis of $Mo(CO)_5L$ compounds which have charge transfer maxima at longer wavelength[21,40] using light >305 nm (WG305 filter) was often not noticeably faster. This is not entirely surprising since the rate of photolysis observed will depend on the rate of photoreversal and so on the absorption characteristics of the products. Product absorptions often overlap with bands in the spectrum of the starting material and so it was only in cases where a single product could be obtained fortuitously that a full u.v./visible spectrum of a fragment could be obtained.

Overall photolysis rates are always much less in glasses than in inert gas matrices, even when heavier inert gases (Kr,Xe) are used. An explanation for this is that energy of a photolytic fragment could be transferred to glass molecules to activate vibrations whereas in a monatomic gas matrix transfer of kinetic energy to matrix molecules is more likely to create spaces so that photolytic fragments can separate and so photolysis will be more efficient. Photolysis rates in small molecule matrices (e.g. N_2, CH_4, SF_6) seem to be intermediate between glass and monatomic gas rates as expected.

So far only photolysis products in inert or weakly interacting matrices have been discussed. These are quite different from the products in a strongly interacting matrix. Strongly interacting matrices can be of two types: (a) σ donor (basic) matrix e.g. MTHF or EtOH/MeOH glass or (b) π acceptor e.g. N_2, CO, PF_3, and reactive species generated in them normally react very quickly after production so that the only observable species are compounds including the matrix material. Such compounds are often stable at room temperature and may well be intermediates in room temperature reactions, e.g. $Mo(CO)_5(MTHF)$ which will be an intermediate in any room temperature photochemical reaction of $Mo(CO)_6$ in MTHF solution. Photolysis products in type (a) matrices are derivatives of the parent carbonyls with basic substituents and their i.r. spectra fall into patterns expected for such compounds with a general lowering of CO stretching frequencies as the degree of substitution is increased. An increase of substitution with a non π accepting ligand implies an increase of electron density on the central metal atom of a metal carbonyl system; so substitution and hence photolysis becomes increasingly more difficult as CO's are lost. Again, in MTHF glass, no species with less than three carbonyl groups (except $CpMn(CO)_2(MTHF)$) were observed. As electron density builds up on the central metal the compounds become less stable. For example $Fe(CO)_3(MTHF)_2$ generated in MTHF glass at 77K decomposed between 100 and 120K.

Photoreversal is not observed in strongly interacting matrices, except in the case of $[V(CO)_5(MTHF)]^-$ where the anionic nature of the product probably contributes to its instability.[41] Even thermal reactions occuring after glass softening do not result in complete regeneration of starting material and it seems that compounds such as $Mo(CO)_5(MTHF)$ are actually thermodynamically unstable with respect to some kind of non-carbonyl containing decomposition product. Although this type of decomposition is slow, it still competes with replacement of MTHF with CO in a sealed cell with CO present at room temperature.

The photolysis products in type (b) matrices are more similar to the parent carbonyls in electronic distribution. Since no such matrices were used in this work, they will not be discussed in detail, but it should be noted that reactions with such matrices seem to be much slower than reactions with σ donor matrices, although a direct comparison is not possible because of the 50 degree temperature difference between glass and gas matrix work. For example, $Cr(CO)_5$ can be generated in a CO matrix by photolysis[37] or atomic deposition[28] while $Cr(CO)_5$ in MTHF glass is unknown, yet $Cr(CO)_5(MTHF)+CO$ is unstable with respect to $Cr(CO)_6+MTHF$. Possibly the reason for the apparent very fast reaction of carbonyl fragments with σ donors is the pre-photolytic association of carbonyl and base mentioned earlier.

The use of a strongly interacting matrix will of course modify the i.r. spectra — of both starting material and products in the MTHF case — and the u.v./visible spectra as well. It was found that by using a 1M solution of MTHF in 4:1 methylcyclohexane:isopentane as glass forming solvent that the better resolved i.r. spectra characteristic of hydrocarbon glass could be obtained, but the products **were mainly the same as those** obtained in MTHF glass (i.e. MTHF complexes). In the same way ligands other than MTHF which do not form glasses at 77K could be used in hydrocarbon glass. A similar approach has been used in gas matrix work where NO and CO doped Ar matrices have been used to synthesise compounds such as $Fe(CO)_2(NO)_2$ and $Co(CO)_4$ by photochemical reactions from stable precursors.[42]

The nature of the carbon monoxide lost in photolysis in the matrix could well influence photoreversal and reactions occurring on glass softening. The i.r. spectrum of CO in gas matrices[43,44] and solid neopentane[44] has been examined in great detail and the CO frequency of 2138 cm^{-1} observed in hydrocarbon glass is typical of a small CO polymer. Whether the CO is in fact polymeric or merely perturbed by the closeness of $M(CO)_{n-1}$ type fragments is not known. On glass softening the CO band becomes broader, probably indicating the formation of larger polymeric units. Bands due to uncomplexed CO are very weak relative to the strongest CO stretches in metal carbonyls and so the 'free' CO bands observed in this work were always very weak. In MTHF glass the CO bands were about five times as intense as those observed for corresponding concentrations in hydrocarbon indicating some sort of interaction between CO and MTHF, but the CO frequency (2136 cm^{-1}) in MTHF was not much different from that observed in hydrocarbon.

The possibility that CO is interacting with $M(CO)_{n-1}$ fragments raises the question of whether the primary photolysis products are in fact $M(CO)_{n-1}$ CO where the CO may be bonded through oxygen (isocarbonyl) or sideways bonded like an olefin as has been suggested recently.[28] However, in $Fe(CO)_5$ photolysis, where the primary product is almost certainly $Fe(CO)_4$(alkane),[37] the CO frequency is 2138 cm^{-1}; the same as in all other systems examined in hydrocarbon glass. Therefore, if there is interaction between ejected CO and the other fragment, this is very weak with CO functioning as a less efficient ligand than saturated hydrocarbon. From results of studies in a range of gas matrices, Perutz is of the opinion that $Cr(CO)_5 \cdots CO$ interactions are only important in matrices doped with CO or pure CO.[90]

In photolysis of $Fe(CO)_5$, $LM(CO)_5$, and $LFe(CO)_4$ there are two distinct types of CO group which can be lost, assuming the molecule retains a structure similar to its ground state during the photolysis process. In $Fe(CO)_5$ there is a major rearrangement of either starting material or more likely photolytic fragment to produce a severely distorted tetrahedral $Fe(CO)_4$.[29] In the other two cases the fragments $LM(CO)_4$ ($L=PR_3$ etc., M=Cr, Mo, W) and $LFe(CO)_3$ ($L=PR_3$,[45] MTHF, etc.) have structures based on the parent compounds. $LM(CO)_4$ is square pyramidal (octahedral with one vacant site) and $LFe(CO)_3$ is trigonal pyramidal (trigonal bipyramidal with one vacant site). It has been suggested that in photolysis of transition metal complexes the primary process should be loss of a ligand lying on the axis of lowest ligand field strength (at least in octahedral complexes), and that the ligand of lowest ligand field strength on this axis should be lost preferentially.[46,47] This seems reasonable if photolysis occurs via the lowest energy excited state, and at least the first part of the rule has been shown to hold for photochemical substitution of Co (III) and Rh (III) amine complexes with water.[48] Since CO is placed high in the spectrochemical series, it is likely that almost any ligand other than CO should be preferentially expelled or, if this is not possible because of matrix conditions, at least the CO trans to the ligand should be expelled. In $Co(CN)_5X^{3-}$ ($X=I^-,SCN^-,N_3^-$) which are isoelectronic with $Cr(CO)_6$ it is always the weaker field ligand X^- which is expelled in photochemical reactions in aqueous solution.[49] These reactions proceed through an intermediate $Co(CN)_5^{2-}$ isoelectronic with $Cr(CO)_5$, but in aqueous solution are complicated by ion pair and ionic strength effects and competing thermal reactions and so are not directly comparable with $Cr(CO)_6$ photolysis in organic solvents. It has also been suggested that the lowest energy charge transfer transition in $LM(CO)_5$ complexes is a transition into the π^* orbitals of the four equatorial CO groups.[21] Which of these suggestions is correct depends on the relative positions of σ^* and π^* orbitals which will depend on the nature of the ligands other than CO and the metal a.o. energy levels, and so probably there is no generalisation applicable. However, the photolysis of both $LM(CO)_5$ and $(MTHF)Fe(CO)_4$ can be interpreted in terms of loss of CO trans to the ligand being the most important primary process.

Conclusion

It may seem that the glass photolysis technique described in this chapter is a poor method for studying reactive fragments and photolytic reactions as many of the details of the photolyses are unknown and often the products can only be identified by comparison with gas matrix studies, but, as has been previously stated, reaction conditions in glass are much closer to those normally employed in preparative chemistry than an inert gas matrix. Species which interact with a hydrocarbon matrix at 77K will almost certainly interact with hydrocarbon solvent at room temperature and so if these species are intermediates in room temperature reactions they will almost certainly be present in their hydrocarbon complex form.

Another important advantage of the glass technique is its versatility. A great variety of potential reactants can be included very easily in an inert or weakly interacting glass and can be examined using the fairly simple apparatus described in the experimental chapter. In the present study i.r. spectroscopy was used as the main method of observation and the apparatus was chosen accordingly. However, there is no reason why the same technique should not be used with other methods of reaction monitoring (Glass techniques are already common in e.s.r. and luminescence studies.). Photochemistry in glasses can be thought of as a method of controlling photoreactions rather than a technique for the study of simple reactive species, which inert gas matrix isolation obviously is. However, care must always be taken when applying results of glass photolysis studies to preparative problems and there may be serious practical problems in scaling up glass reactions for preparative chemistry.

For references 50-55 see Appendix.

CHAPTER 2

PENTACARBONYLIRON

Introduction

Many of the reactions of pentacarbonyliron, both thermal and photochemical , can be explained by mechanisms involving the step $Fe(CO)_5 \longrightarrow Fe(CO)_4 + CO$.

e.g. $2Fe(CO)_5 \longrightarrow Fe_2(CO)_9 + CO$

$Fe(CO)_5 + PR_3 \longrightarrow Fe(CO)_4PR_3 + CO$ [56,57]

Kinetic evidence for the existence of $Fe(CO)_4$ has been obtained in studies of the photochemical exchange of CO with ^{14}CO in $Fe(CO)_5$ in hydrocarbon solution,[58] in the thermal reaction of $Fe_2(CO)_9$ with phosphines in hydrocarbon solution,[59] and in thermal reactions of $Fe(CO)_4$(olefin) with CO.[60] Some thermal reactions of $Fe(CO)_5$, however, go through a six coordinate intermediate,[31,61] e.g. $Fe(CO)_5 + I_2 \longrightarrow Fe(CO)_4I_2 + CO$, but in photochemistry the dissociation of one CO has been accepted as the primary process. In 1962 Stolz, Dobson, and Sheline[14] looked at the primary photolysis of $Fe(CO)_5$ in 4:1 methylcyclohexane:isopentane (mch:ip) glass at 77K and observed trapped CO and three new i.r. bands at 1990, 1980, and 1946 cm^{-1} and noted the appearance of $Fe_2(CO)_9$ bands on glass softening. However, it was not possible to assign a structure to the CO deficient fragment responsible for these three new i.r. bands. (At the time when this research was begun it had been suggested that unsaturated carbonyl fragments would assume the structure of highest possible symmetry in the ground state,[12] and so it was thought that $Fe(CO)_4$ would be tetrahedral, or possibly square planar analogous to isoelectronic $Ni(CN)_4^{2-}$.[62]) Since Sheline's work kinetic evidence had been obtained which showed that $Fe(CO)_4$, produced by flash photolysis at room temperature,[63] was extremely reactive, and so a re-examination of the $Fe(CO)_5$/4:1 mch:ip system was thought necessary.

Photolysis in Hydrocarbon Glass.

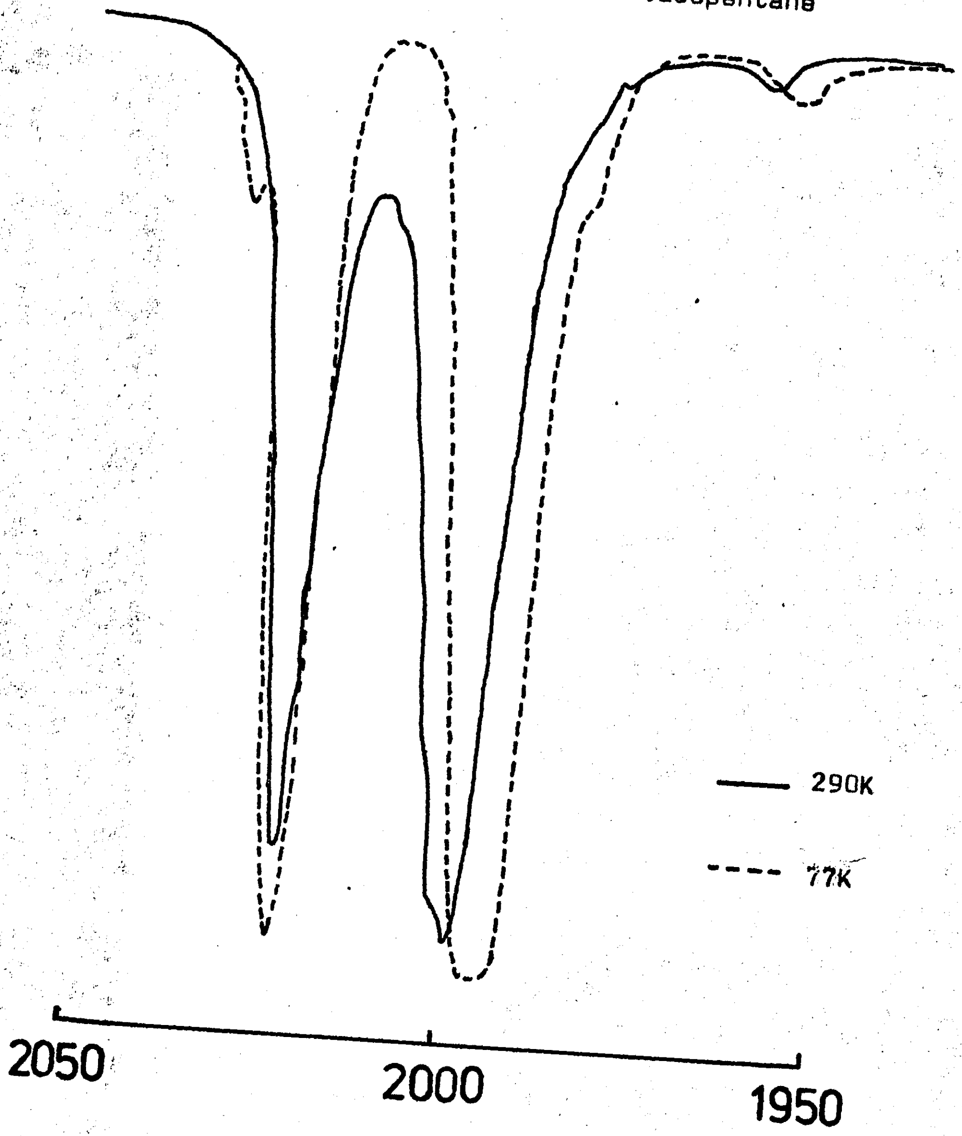
Changes in the CO stretching region of the i.r. spectrum of $Fe(CO)_5$ in 4:1 mch:ip were apparent on cooling to 77K. The A_2'' band at 2023 cm^{-1} develops a shoulder on the high frequency side and the E' band at 2000 cm^{-1} changes shape, develops a shoulder on the low frequency side, and shifts to 1994 cm^{-1}. The band at 1964 cm^{-1} due to an A_1 mode of equatorially substituted $Fe(CO)_4(^{13}CO)$ also shifts to 1958 cm^{-1} (see fig. 2-1). These effects are mostly consistent with changes expected to occur on cooling isolated $Fe(CO)_5$ molecules. The shoulders both correspond to modes of $Fe(CO)_4(^{13}CO)$ predicted but not observed by Bor in room temperature spectra in n-heptane solution.[64]

Table 2-1

Observed Frequency	Predicted Frequency[64]
2029	2028.6 (A_1 mode of ax. $Fe(CO)_4(^{13}CO)$)
	2027.2 (A_1 " " eq. ")
1985	1987.4 (A_1 " " ax. ")

The 2029 cm^{-1} shoulder is the more intense as expected. Although the E' mode of $Fe(CO)_5$ shows an apparent increase in half width, examination of

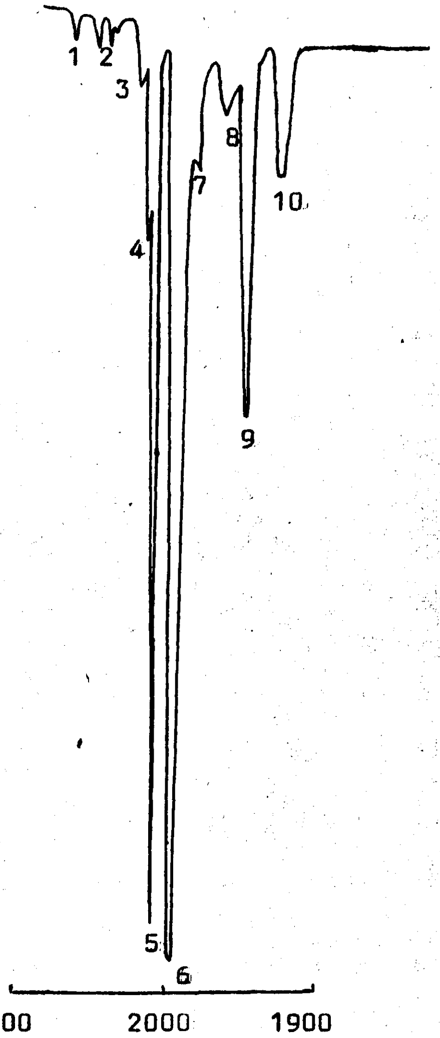
Figure 2-1: $Fe(CO)_5$ in 4:1 methylcyclohexane:isopentane



the spectrum near the base line shows that the band has actually sharpened and the change of shape is probably due to a lifting of the degeneracy of the two components of the E' mode because of a slight distortion from D_{3h} symmetry. It is unlikely that the incipient splitting is due to $Fe(CO)_5$ in different types of sites in the glass as none of the other bands are split, but the $Fe(CO)_5$ molecule is probably distorted by the glass matrix. $Fe(CO)_5$ in a methane matrix at 20K shows similar behaviour.[39] It is also unlikely that any of the spectral changes are due to aggregates of $Fe(CO)_5$ since no polymeric iron carbonyls are observed in the glass after photolysis. All the changes in spectra detailed above were reversible on warm up.

Photolysis of $Fe(CO)_5$ in 4:1 mch:ip with unfiltered light showed initially four new i.r. bands at 2084, 1988, 1977, and 1944 cm^{-1}, the three lowest frequency bands being similar to those observed by Sheline, and trapped CO at 2138 cm^{-1}. On prolonged photolysis a further two bands appeared at 2038 and 1925 cm^{-1}. Irradiation with pyrex filtered light produced further bands at 2100, 2078, and 1961 cm^{-1} (fig. 2-2). On irradiation with WG 335 filtered light (for characteristics of filters see experimental section) all the above mentioned bands disappeared slowly as $Fe(CO)_5$ was regenerated. During glass softening experiments the bands at 2038 and 1925 cm^{-1} disappeared first around 96K and then the other bands collapsed around 105K to give mainly $Fe(CO)_5$ although traces of $Fe_2(CO)_9$ (absorptions at 2065 and

Figure 2-2: $Fe(CO)_5$ in 4:1 mch:ip after 60 min. irradiation with pyrex filter



1	2138 cm^{-1}	trapped CO
2	2100, 2084, and 2078 cm^{-1}	
3	2038 cm^{-1}	$Fe(CO)_3$
4	2029 cm^{-1}	$Fe(CO)_4(^{13}CO)$
5	2023 cm^{-1}	$Fe(CO)_5$
6	1992 cm^{-1}	$Fe(CO)_5$+$Fe(CO)_4$(alkane)
7	1977 cm^{-1}	$Fe(CO)_4$(alkane)
8	1961 cm^{-1}	$Fe(CO)_4$?
9	1944 cm^{-1}	$Fe(CO)_4$(alkane)
10	1925 cm^{-1}	$Fe(CO)_3$

1845 cm^{-1}) and sometimes $Fe_3(CO)_{12}$ (absorptions at 2045 and 1835 cm^{-1}) could be observed at 195K and room temperature. In all cases photolysis was very slow compared to similar work in inert gas matrices at 20K. For example Poliakoff[39,65] found that 5 min. photolysis of $Fe(CO)_5$ in a methane matrix at 20K with a medium pressure Hg arc gave $Fe(CO)_3$ as a major product, whereas in this work $Fe(CO)_3$ only began to appear after 30 min. photolysis. As photolysis continues the system tends to a steady state, apparently governed by equilibria of the type $Fe(CO)_5 \rightleftharpoons$ primary product +CO $\rightleftharpoons$ secondary product +2CO, where the forward reactions are favoured by higher energy light and the back reactions by lower energy light. U.V./visible spectra of $Fe(CO)_5$+product mixtures in glass consisted of broad,overlapping bands from which very little could be deduced. Possibly complete photolysis of $Fe(CO)_5$ in the glass could be accomplished by irradiation with suitable monochromatic light, but since monochromatic filters transmit only around 20% of the total incident light at their maximum transmission frequency, such experiments would necessarily be very slow and were not carried out.

The two bands at 2038 and 1925 cm^{-1}, produced on prolonged photolysis under all irradiation conditions used, form a pattern typical of a C_{3v} tricarbonyl compound[66] with a sharp A_1 band (2038 cm^{-1}) and a broader E band (1925 cm^{-1}) at lower frequency. The flat topped appearance of the E band suggests that it is in fact split into two components which are not resolved. The most probable assignment for these two bands is to a pyramidal $Fe(CO)_3$ fragment and this was confirmed by Poliakoff[39] who observed $Fe(CO)_3$ in methane, argon, krypton, and xenom matrices and confirmed his assignment and the C_{3v} structure by force constant calculations on ^{13}CO substituted $Fe(CO)_3$. No estimate of the $C-\widehat{Fe}-C$ angle from the relative intensities of the A_1 and E modes could be made here because the A_1 band always overlaps the A_2'' band of $Fe(CO)_5$. A major difference between the spectra of $Fe(CO)_3$ in hydrocarbon glass and in gas matrices is the incipient splitting of the E band. The shape of this band is similar to the E' band of $Fe(CO)_5$ and the splitting is most probably also due to distortion of $Fe(CO)_3$ from C_{3v} symmetry by the glass. Table 2-2 shows a comparison of Cotton-Kraihanzel force constants for $Fe(CO)_3$ in glass with those calculated by Poliakoff for $Fe(CO)_3$ in gas matrices.[39]

Table 2-2

Matrix	A_1	E	K	k_i	Ref.
4:1 mch:ip	2038	1925	15.57	0.60	This work
CH_4	2040.1	1930.4	15.627	0.586	39
Xe	2037	1927	15.57	0.58	39
Kr	2044	1933	15.67	0.60	39
Ar	2042±2	1935.6	15.70	0.6	39

K,k_i units: md/A

Since bands observed earlier in the photolysis vary in intensity with different irradiation conditions used, it is evident that there are at least two primary products with possible interconversion of these products. The four bands at 2084, 1988, 1977, and 1944 cm^{-1} appear to belong to the same species, but their relative intensities are very difficult to estimate because the 2084 cm^{-1} band is weak and the 1988 cm^{-1} band overlaps with the E' band of $Fe(CO)_5$. The bands at 2100, 2078, and 1961 cm^{-1} are all weak. At first it was thought that the two species could be due to two low symmetry isomers of $Fe(CO)_4$, but without facilities for isotopic labelling studies this could not be verified.

Poliakoff and Turner[29] have identified a species $Fe(CO)_4(CH_4)$ in methane and methane doped argon matrices and this has a spectrum with four bands similar to those observed for the product in glass after unfiltered irradiation. They have also observed this species and assign it as $Fe(CO)_4$(glass). $Fe(CO)_4$ itself has also been observed in SF_6 and other matrices and its structure has been confirmed as C_{2v} distorted tetrahedral by force field calculations on ^{13}CO substituted molecules.[29,65] $Fe(CO)_4$ also showed significant interaction with a xenon matrix. $Fe(CO)_4(CH_4)$ appears to have a structure which is best described as distorted equatorially substituted trigonal bipyramidal (C_{2v}) from force field calculations on isotopically substituted species. Table 2-3 is a comparison of the observed frequencies of $Fe(CO)_4$, $Fe(CO)_4(CH_4)$, and the $Fe(CO)_4$(alkane) species observed in the glass.

Table 2-3

$Fe(CO)_4$ [a,29]	$Fe(CO)_4(CH_4)$ [a,29]	$Fe(CO)_4$(glass) [b,c]
1993.0 1991.6 (vs)	2088 (vw)	2084 (vw)
1985 (m)	1995.6 1991.0 (s)	1988 (s)
1966.5 (s)	1984.2 1981.3 (w)	1977 (w)
	1953 1949.8 (vs)	1944 (vs)

a CH_4 matrix at 20K b 4:1 mch:ip glass at 77K

c this work

Poliakoff and Turner also proposed interconversion $Fe(CO)_4 \rightleftharpoons Fe(CO)_4(CH_4)$ in the visible light of the i.r. spectrometer beam and so an experiment was conducted with a germanium filter between the spectrometer source and the sample cell. This caused a considerable reduction in intensity of the i.r. beam and the adjustments of the spectrometer required to compensate for this caused a loss of resolution in the spectra. Even with the germanium filter in the i.r. beam the main species detected was $Fe(CO)_4$(glass), although traces of $Fe(CO)_4$ may have been present since most of the $Fe(CO)_4$ bands would be masked by $Fe(CO)_5$ and $Fe(CO)_4$(glass) bands. In this experiment the 2100 cm^{-1} but not the 2078 cm^{-1} band was observed. Removal of the germanium filter and re-running of the spectrum did not show any significant increase in $Fe(CO)_4$(glass) concentration. Presumably the inclusion of the filter would be much less important here than in Poliakoff's case as the i.r. source in a PE 457 or PE 577 is much less intense than in a Grubb-Parsons Spectromajor, and photolysis, and so presumably photoinitiated association, is much slower in glass than in gas matrices. The 1961 cm^{-1} band observed in the photolysis with pyrex filtered light is closer to the 1966.5 cm^{-1} band of $Fe(CO)_4$ than any other observed band and the 2100 cm^{-1} band is fairly close to the frequency Poliakoff predicted for the highest frequency, unobserved band of $Fe(CO)_4$; so it may be that the species responsible for these two bands is $Fe(CO)_4$ or something very similar to it. The 2078 cm^{-1} band was only observed on irradiation with pyrex filtered light and overlapped with the 2084 cm^{-1} band of $Fe(CO)_4$(glass) to form a doublet (see fig. 2-2). On prolonged irradiation the 2078 cm^{-1} component became the more intense; so it may well be due to some form of $Fe(CO)_4$(glass).

There seems little doubt that the main primary product observed is $Fe(CO)_4$(alkane), but very little information about the iron to alkane bond can be deduced either from glass or gas matrix experiments. However, a noteworthy point is the 'sharpness' of the $Fe(CO)_4$(glass) bands, e.g. the 1944 cm^{-1} band of $Fe(CO)_4$(glass) $\delta\nu_{\frac{1}{2}}$=6.5 cm^{-1}; A_2'' band of $Fe(CO)_5$ in glass $\delta\nu_{\frac{1}{2}}$=6.0 cm^{-1}. It would be reasonable to expect broad bands if $Fe(CO)_4$

reacts with a number of different sites in the glass to form several closely related species. It therefore seems likely that there is specific reaction between $Fe(CO)_4$ and a particular site in a glass molecule. The similarity between the spectra of $Fe(CO)_4$(glass), $Fe(CO)_4(CH_4)$, and $Fe(CO)_4Xe$ suggests that oxidative insertion of $Fe(CO)_4$ into a C-H or C-C bond does not occur. However, it is possible that there is some specific interaction between $Fe(CO)_4$ and a C-H bond so that the metal achieves an eighteen electron configuration by forming a two electron three centre bond analogous to those proposed by Cotton et al.[67] in compounds of the type $(Et_2B(pyrazolyl)_2)Mo(CO)_2(\pi$-allyl). This type of interaction between $Fe(CO)_4$ and a methyl group in methylcyclohexane or isopentane could give a species with four sharp i.r. bands similar to $Fe(CO)_4(CH_4)$, but there is no reason to rule out species in which the glass is bound through a secondary or tertiary hydrogen. In $(Et_2B(pyrazolyl)_2)Mo(CO)_2(\pi$-allyl) it is a carbon α to the boron which approaches close to the metal. Experiments which could possibly give more information on $Fe(CO)_4$ to alkane bonding are photolysis in 1:1 decalin:methylcyclohexane glass, which is about 0.3 molar in $-CH_3$ where 4:1 mch:ip is about 10 molar, and irradiation in a range of saturated hydrocarbon solvents at room temperature monitoring changes in the solvent by g.l.c. No i.r. bands which could be definitely assigned to C-H-Fe breathing modes were observed, but these are expected to be very weak and broad relative to CO stretches and could easily occur in the same region of the spectrum and so be mistaken for or masked by CO stretches.

From the above results it would appear that the most likely intermediate in room temperature photochemical reactions of $Fe(CO)_5$ is not $Fe(CO)_4$ but $Fe(CO)_4$(alkane) (in alkane solution), the alkane being subsequently displaced by a more suitable ligand, CO, or $Fe(CO)_5$ to form $Fe(CO)_4L$, $Fe(CO)_5$, or $Fe_2(CO)_9$. $Fe(CO)_4L$ may then photolyse further to give $Fe(CO)_3L_2$. Another possible path for the formation of $Fe_2(CO)_9$ and $Fe(CO)_3L_2$ is through dimerisation of $Fe(CO)_4$ to $Fe_2(CO)_8$. This of course cannot occur in the glass. No bands due to $Fe_2(CO)_8$[68] were observed on softening of $Fe(CO)_4$(alkane) containing glasses and photochemical reactions of $Fe(CO)_5$ with phosphines and phosphites at room temperature usually give predominantly $Fe(CO)_4L$ and $Fe_2(CO)_9$ in the initial stages[57]; so $Fe(CO)_4$(alkane) probably does not dimerise. However, in thermal reactions of $Fe_2(CO)_9$ with phosphines at room temperature, where $Fe(CO)_4$ is thought to be an intermediate, $Fe(CO)_3L_2$ and $Fe_3(CO)_{12}$ are always formed; so $(Fe(CO)_4)_n$ polymers are probably important in this case. Since $Fe_2(CO)_9$ is insoluble in hydrocarbon, the above reactions may take place on the $Fe_2(CO)_9$ surface, and so there may not be any $Fe(CO)_4$ or $Fe(CO)_4$(alkane) present in solution in the reaction mixture.

Starting solutions used in this work were typically 10^{-2}M in $Fe(CO)_5$

i.e. a molecule:molecule ratio of about 1:700 solute:glass, or a ratio of about 1:4200 solute:carbon atoms in the glass. The latter ratio is probably more comparable with the matrix ratios quoted by other workers[29,69] for monatomic gas and small molecule matrices, and it is not surprising that no polymeric species are formed by photolysis at this dilution. However, considerable interaction between $Fe(CO)_5$ and impurities introduced into the glass was apparent on freezing and will be discussed later.

Photolysis in Reactive Glasses

Irradiation in ethers, especially tetrahydrofuran (THF), and subsequent addition of a ligand is a common preparative route to specifically monosubstituted derivatives of group VI hexacarbonyls and arene metal tricarbonyls[71-73]. However, this method does not seem to have been used for the preparation of $Fe(CO)_4L$ compounds from $Fe(CO)_5$, probably because of the ready formation of $Fe_2(CO)_9$ from $Fe(CO)_5$ irradiated in THF solution. A likely path for this reaction is $Fe(CO)_5+THF \xrightarrow{h\nu} Fe(CO)_4(THF)+CO \xrightarrow{Fe(CO)_5} Fe_2(CO)_9+THF$. Since the properties of $Fe(CO)_4(THF)$ were unknown and it was hoped that this compound would resemble the $Fe(CO)_4$ fragment closely, photolysis of the $Fe(CO)_5$/2-methyltetrahydrofuran (MTHF) system at 77K was investigated.

In some very recent work by Cotton and Troup[70] $Fe(CO)_4$(pyridine) and $Fe(CO)_4$(pyrazine) have been prepared by reaction of $Fe_2(CO)_9$ with the respective ligands in THF solution and there is circumstantial evidence that $Fe(CO)_4(THF)$ is an intermediate in these reactions. $Fe(CO)_4(THF)$ is thought to be generated spontaneously from $Fe_2(CO)_9$ and THF at room temperature under a CO atmosphere. However, exclusion of light in the experiment is not specifically mentioned and so the reaction is possibly photochemical. The final products of the $Fe_2(CO)_9$/THF reaction under a CO atmosphere are $Fe(CO)_5$ and $Fe_3(CO)_{12}$, the latter probably being produced by the reaction of $Fe(CO)_4(THF)$ with $Fe_2(CO)_9$ as $Fe(CO)_4(THF)$ does not trimerise in the absence of $Fe_2(CO)_9$.

The spectrum of $Fe(CO)_5$ in MTHF was considerably broader than that recorded in hydrocarbon solution and the A_2'' band appeared only as a shoulder on the broad E' band at room temperature. On cooling to 77K the bands resolved, but both split into two components (fig. 2-3). The A_2'' band (2021 cm^{-1} in room temperature spectra) shifts slightly to 2023 cm^{-1} and develops an intense shoulder at 2032 cm^{-1}. The E' mode (about 1996 cm^{-1} at room temperature) resolves into two components of equal intensity at 1994 and 1987 cm^{-1}. A further weak band at 2120 cm^{-1} was also observed. These splittings are not due to matrix effects since similar splittings were observed in hydrocarbon glasses doped with MTHF or THF but not in pure hydrocarbon glass. In the doped glasses the spectra were sharper but the splittings were still evident. On freezing a solution of $Fe(CO)_5$ (10^{-2}M)

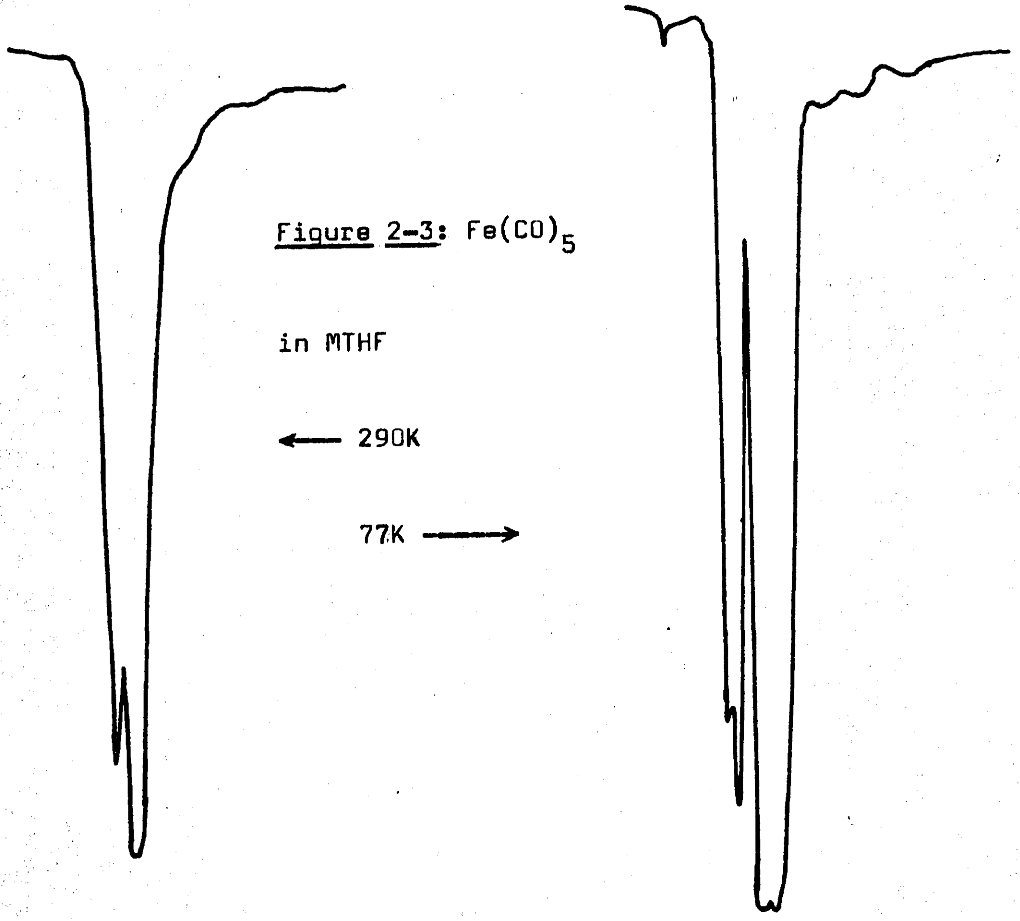


Figure 2-3: $Fe(CO)_5$

in MTHF

← 290K

77K →

and MTHF (1M) in 4:1 mch:ip almost all the $Fe(CO)_5$ in the glass was in the form which is present in MTHF glass, and even with an MTHF concentration of 10^{-2}M detectable amounts of modified $Fe(CO)_5$ were present. A controlled cooling experiment on 10^{-2}M $Fe(CO)_5$ and 1M THF in isopentane in a cell with AgCl windows showed major changes in the spectrum beginning around 235K and a considerable amount of interaction by 118K. These spectra also showed major changes in the 700-600 cm^{-1} region. Room temperature spectra showed two fairly broad bands at 641 and 613 cm^{-1} assigned to Fe-C-O bends (E' and A_2'' respectively)[76]. On cooling these bands gradually sharpened and shifted to 643 and 617 cm^{-1}. A new band at 660 cm^{-1} developed around 150K and by 118K had comparable intensity with the other two and had shifted to 664 cm^{-1} with shoulders at 669 and 655 cm^{-1}. There was no reduction in intensity of the other two bands during the growth of this band. The position of this band does not correspond to any Raman active or inactive fundamental mode of $Fe(CO)_5$[74].

It seems likely, therefore, that there is coordination of MTHF or THF to $Fe(CO)_5$ to form a six coordinate complex. Complexes of $Fe(CO)_5$ with Br_2 have been prepared by precipitation from heptane solution at 195K and $Fe(CO)_5I_2$ has been proposed as an intermediate in the oxidation of $Fe(CO)_5$ with I_2 in hexane,[31] but in these cases the halogen molecule is thought to add oxidatively across $Fe(CO)_5$. In this case a six coordinate structure based on octahedral coordination about iron at first seems plausible, but the i.r. band pattern in the CO stretching region does not resemble that of C_{4v} $M(CO)_5L$ and there is one δM–C–O band too many. A structure which fits the spectra better is a C_{2v} form with MTHF in a site in the equatorial plane of $Fe(CO)_5$ but farther from the metal than the carbonyl carbon atoms. This structure has five i.r. active CO stretches and ten δM–C–O motions, three of which correlate to the $Fe(CO)_5$ modes in the 700–600 cm^{-1} region. An analogous molecule for which frequencies in the CO stretching region have been calculated and observed[58,64] is vic-$(^{13}CO)_2Fe(CO)_3$ although modes involving motion of ^{13}C will have frequencies about 30 cm^{-1} lower in that case. Table 2-4 shows a comparison of the observed frequencies of $Fe(CO)_5(THF)$ with those observed by Noack and Ruch for vic-$(^{13}CO)_2Fe(CO)_3$

in heptane at 253K together with a correlation of the i.r. active modes of D_{3h} and C_{2v}.

Table 2-4

D_{3h}	C_{2v}	(I)	(II)	
A_2'' —	B_1	$Fe(CO)_5(THF)$	vic-$(^{13}CO)_2Fe(CO)_3$	
E'	A_1	----*	2098	A_1
	B_2	2032	2023	A_1
		1995	1976	A_1
		1985	1955	B_2
		2023	2023	B_1

* not observed for $Fe(CO)_5(THF)$ in isopentane, but cf. 2120 cm^{-1} band in $Fe(CO)_5$/MTHF.

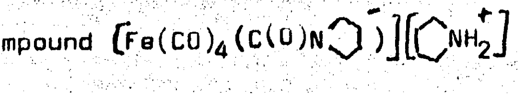
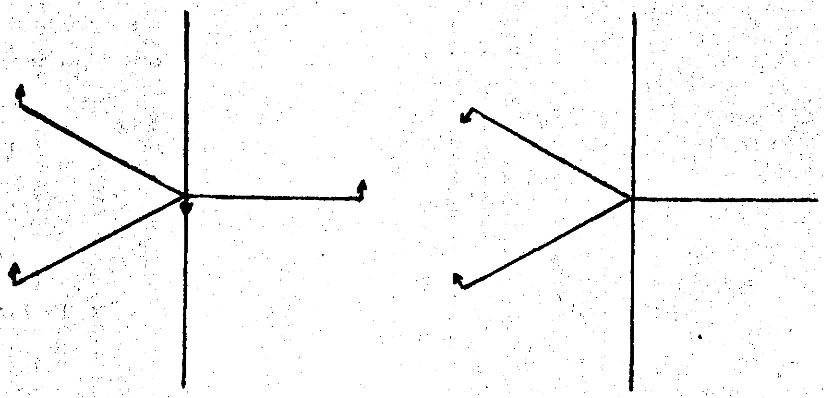
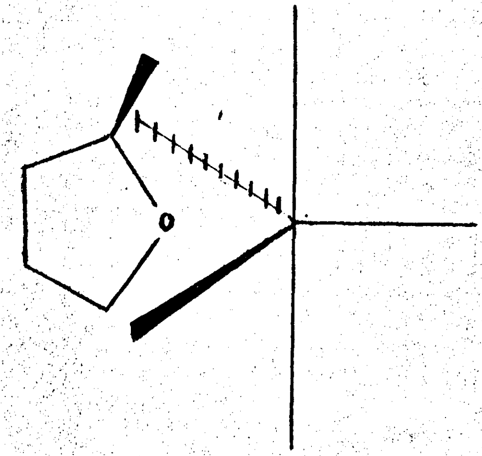
The 1976 (A_1) and 1955 cm^{-1} (B_2) modes of (II) correlate with the E' mode of $Fe(CO)_5$ and hence with the 1995 and 1985 cm^{-1} modes of (I). Since these modes of (II) involve motion of ^{13}CO groups, their frequencies are considerably lower. The B_1 mode of (II) correlates directly with the A_2'' mode of $Fe(CO)_5$ and has the same frequency as the corresponding mode of (I). The two highest frequency A_1 bands of (I) and (II) correlate with the Raman active A_1' modes of $Fe(CO)_5$ observed at 2114 and 2031 cm^{-1} in the liquid[75]. Again, both these bands occur at lower frequency in (II) because of the involvement of ^{13}CO motion in the vibrations. Since vic-$(^{13}CO)_2Fe(CO)_3$ was not isolated it is impossible to compare band intensity patterns of (I) and (II), but on frequency data alone it seems that they are comparable in structure and electronic distribution about iron. The coordination of the ether may well be to one or more carbonyl carbon atoms rather than to the metal and this would be expected to produce dramatic changes in the δFe-C-O region of the spectrum. The two bands at 664 and 643 cm^{-1} in (I) are probably components of the E' mode of $Fe(CO)_5$ which occurs at 641 cm^{-1} at room temperature. The shoulders on the 664 cm^{-1} band are probably solvent absorptions (isopentane has an absorption around 670 cm^{-1} at room temperature) due to the temperature difference between the sample and reference cells. The A_2'' band at 617 cm^{-1} is hardly affected by cooling. This is consistent with the coordination of the ether in the equatorial plane since the E' mode is an in-plane bend of the equatorial carbonyls (ν_{11}) while the A_2'' mode is a deformation of the equatorial carbonyls perpendicular to the plane (ν_9) (see fig. 2-4).[76] The structure shown in fig. 2-4 cannot be verified, but seems most likely on i.r. evidence alone. Nucleophilic attack on carbon is thought to be the first step in the reaction of some secondary amines with $Fe(CO)_5$ and, in the case of pyrrolidine, a compound  can be

Figure 2-4:



$\nu_9(A_2'')$ $\nu_{11}(E')$ one component

Symmetry coordinates for δM-C-O modes of $Fe(CO)_5$ in the 600-700 cm^{-1} region.[76]



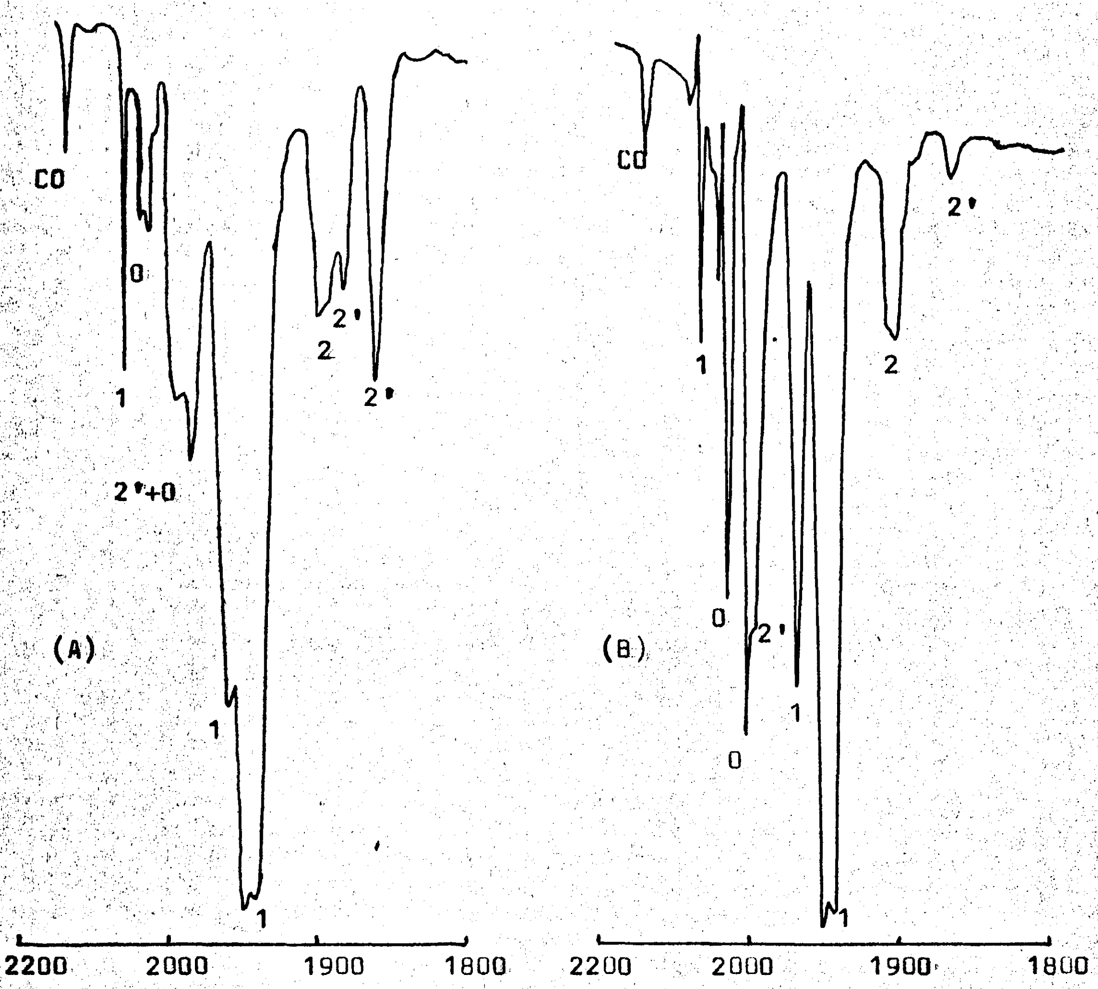
Possible structure for $Fe(CO)_5$(MTHF)

isolated from polar solvents[77]. This has an i.r. spectrum typical of an axially substituted $Fe(CO)_4L$ compound. Similar effects with $Fe(CO)_5$ and triethylamine and triisopropylphosphine will be discussed later.

Photolysis of $Fe(CO)_5$ in MTHF glass showed the expected stepwise loss of CO, but photolysis was very much faster than in hydrocarbon glass. Using WG305 filtered light almost complete photolysis was attained in 15 min. Because of the pre-coordination of MTHF photolysis is much more efficient here since whenever a CO is expelled only an intramolecular rearrangement is required to produce the ground state structure of $Fe(CO)_4$(MTHF) and so recombination with escaped CO is unlikely. Also $Fe(CO)_4$(MTHF) is stable enough to prevent photoreversal on irradiation with lower energy light. In 4:1 mch:ip glass doped with MTHF photolysis is also relatively fast producing similar species to those produced in pure MTHF together with some $Fe(CO)_4$(alkane). Bands due to CO in MTHF glass are about five times as intense as those for corresponding concentrations in hydrocarbon glass, indicating a considerable interaction between CO and MTHF although the frequency (2136 cm^{-1}) of the CO stretch is not much different from that in hydrocarbon. The enhancement of the intensity of the 'free' CO band is also shown in MTHF doped hydrocarbon.

The primary photolysis product shows four i.r. bands at 2060 (m), 1955 (sh), 1944 (vs), and 1935 cm^{-1}(sh) in pure MTHF and at 2062 (m),

Figure 2-5: $Fe(CO)_{5-n}(MTHF)_n$ n= 0,1,2



2 refers to trans-$(MTHF)_2Fe(CO)_3$; 2' refers to cis-$(MTHF)_2Fe(CO)_3$

(A) pure MTHF glass at 77K

(B) 4:1 mch:ip glass containing 1M MTHF at 77K

1963 (s), 1946 (vs), and 1940 cm^{-1}(sh) in 1M MTHF in 4:1 mch:ip (see fig. 2-5). The spectra have band patterns typical of C_{3v} $Fe(CO)_4L$ compounds where the low frequency E mode is split[56] and so the compound is almost certainly axial $Fe(CO)_4$(MTHF). $Fe(CO)_4L$ complexes where L is a hard base are fairly rare and none of those quoted in the literature has a split E band.[19,56,77-81] The frequencies are approximately similar to those observed by Schubert and Sheline for $Fe(CO)_4$(amine) complexes.[78] Again the splitting of the E band is not a matrix effect as it persists at least up to 121K in 1M MTHF in 4:1 mch:ip and so it seems likely that there is coordination of a second MTHF by $Fe(CO)_4$(MTHF). The possibility that more than one MTHF was coordinated to $Fe(CO)_5$ before photolysis cannot be ruled out, but this is unlikely since the same species is formed no matter what the relative concentrations of $Fe(CO)_5$ and MTHF in hydrocarbon glass. At room temperature $Fe(CO)_4$(MTHF) persists for about 1h. in pure MTHF in a sealed cell with CO present. It shows two bands at 2056 and 1940 cm^{-1} (the lower band is slightly broader than the E' band of $Fe(CO)_5$) which gradually disappear as $Fe(CO)_5$ is regenerated.

Further photolysis led to the appearance of four new bands at 1980, 1895, 1877, and 1855 cm^{-1} in pure MTHF and two bands at 1900 and 1865 cm^{-1} together with a shoulder on the E' band of $Fe(CO)_5$ at 1990 cm^{-1} in 1M MTHF in 4:1 mch:ip. In the doped hydrocarbon the 1900 cm^{-1}

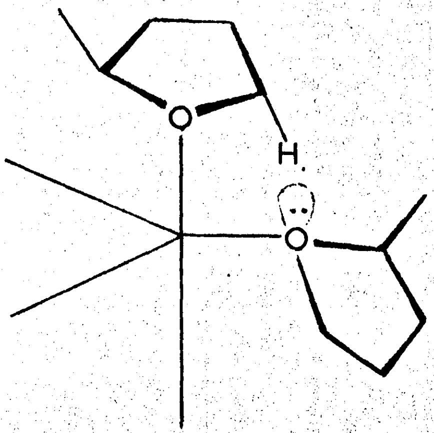
band is the strongest while in pure MTHF the 1855 cm^{-1} band is strongest. On allowing the glass to soften the band at around 1900 cm^{-1} disappeared fastest in both cases at about 90K. The other three bands persisted until about 100K. The band around 1900 cm^{-1} is assigned to trans-$(MTHF)_2Fe(CO)_3$ and the other three bands to the cis isomer. (Here trans- refers to diaxially substituted trigonal bipyramidal molecules, cis- refers to axial-equatorial substitution, and vic- refers to diequatorial substitution .) In pure MTHF the band at 1895 cm^{-1} is broad and irregularly shaped — possibly showing signs of coordinating yet another MTHF molecule, but the coordination to an iron(0) complex with two basic, non-π accepting ligands should be very weak. Reckziegel and Bigorne[56] made a number of mono and trans-disubstituted derivatives of $Fe(CO)_5$ with phosphines, phosphites, and ethylisonitrile and found a linear correlation of the frequencies of correlated modes with the number of substituents. Fig. 2-6 shows a similar correlation diagram for $Fe(CO)_5$/MTHF in hydrocarbon, and the linear relationship is fairly well adhered to confirming the band assignments. The trans compound has D_{3h} symmetry and only one i.r. active mode (E') is predicted, but it might be expected that the A_1' symmetrical stretch would be weakly allowed (by analogy with $Fe(CO)_5$ in MTHF). A shoulder is observed about 2012 cm^{-1} on the low frequency side of the A_2'' band of $Fe(CO)_5$ in a spectrum in MTHF glass where the highest concentration of trans-$(MTHF)_2Fe(CO)_3$ was observed (fig. 2-5) and so this could be the A_1' band. It also fits the Bigorne type correlation diagram very well indeed if the Raman frequency of 2114 cm^{-1} from the liquid spectrum[75] is taken as the frequency of the highest frequency A_1' mode of $Fe(CO)_5$ in MTHF glass. The other compound, however, shows bands at frequencies below those predicted by the correlation diagram for a cis disubstituted compound. This is consistent with Bigorne's observations on substituted group VI hexacarbonyls,[82] and is reasonable because the linear correlation depends on there being little or no change in the geometry of the molecule on substitution and a cis disubstituted species will always be more crowded and hence more distorted than its trans counterpart. Of course there is no correlation between a C_{3v} monosubstituted compound and a vic (C_{2v}) disubstituted compound. The intensity ratio of the 1877 and 1855 cm^{-1} bands suggests that they are due to a cis rather than a vic isomer since in the vic case the B_1 band is normally about three times as intense as the low frequency A_1 band and at higher frequency than it,[83,84] but, since disubstituted $Fe(CO)_5$ derivatives with ether ligands are hitherto unknown, the possibility of a vic isomer cannot be ruled out. It is surprising that the trans isomer is not the most thermally stable since poor π acceptor substituents are thought to prefer axial sites in substituted $Fe(CO)_5$[56,70,83] and MTHF is certainly one of the worst π acceptors ever substituted into $Fe(CO)_5$. In 4:1 mch:ip the bands at 1990 and 1865 cm^{-1} actually grow as the 1900 cm^{-1} band disappears and another band at 1882 cm^{-1} appears on glass softening; so the trans isomer is actually converted to cis by thermal isomerisation. Exceptions to the rule that poorest π acceptors take up axial positions in the trigonal bipyramid occur where the ligand is chelating or where steric factors are more important than electronic. For example $[(CF_3)_2P(OMe)]_2Fe(CO)_3$ is vic because the ligand is only slightly different from CO in π acceptor character and so shows preference for the less crowded equatorial sites.[83] Similarly, (diphos)$Fe(CO)_3$ is vic rather than cis for steric reasons.[56] However, since MTHF substitutes axially in the first place it is unlikely that steric factors are the reason for the enhanced stability of the cis isomer. More likely is some interaction between coordinated MTHF molecules. For instance coordination of the oxygen will increase its electron withdrawing power and so activate the hydrogens on the α carbon, and so there is a possibility of hydrogen bonding between adjacent MTHF molecules. If this is the case it can only occur 'one way' for steric reasons (see fig. 2-7).

Another interesting observation is that proportionately more

Figure 2-7:

Possible structure

for cis-$Fe(CO)_3(MTHF)_2$

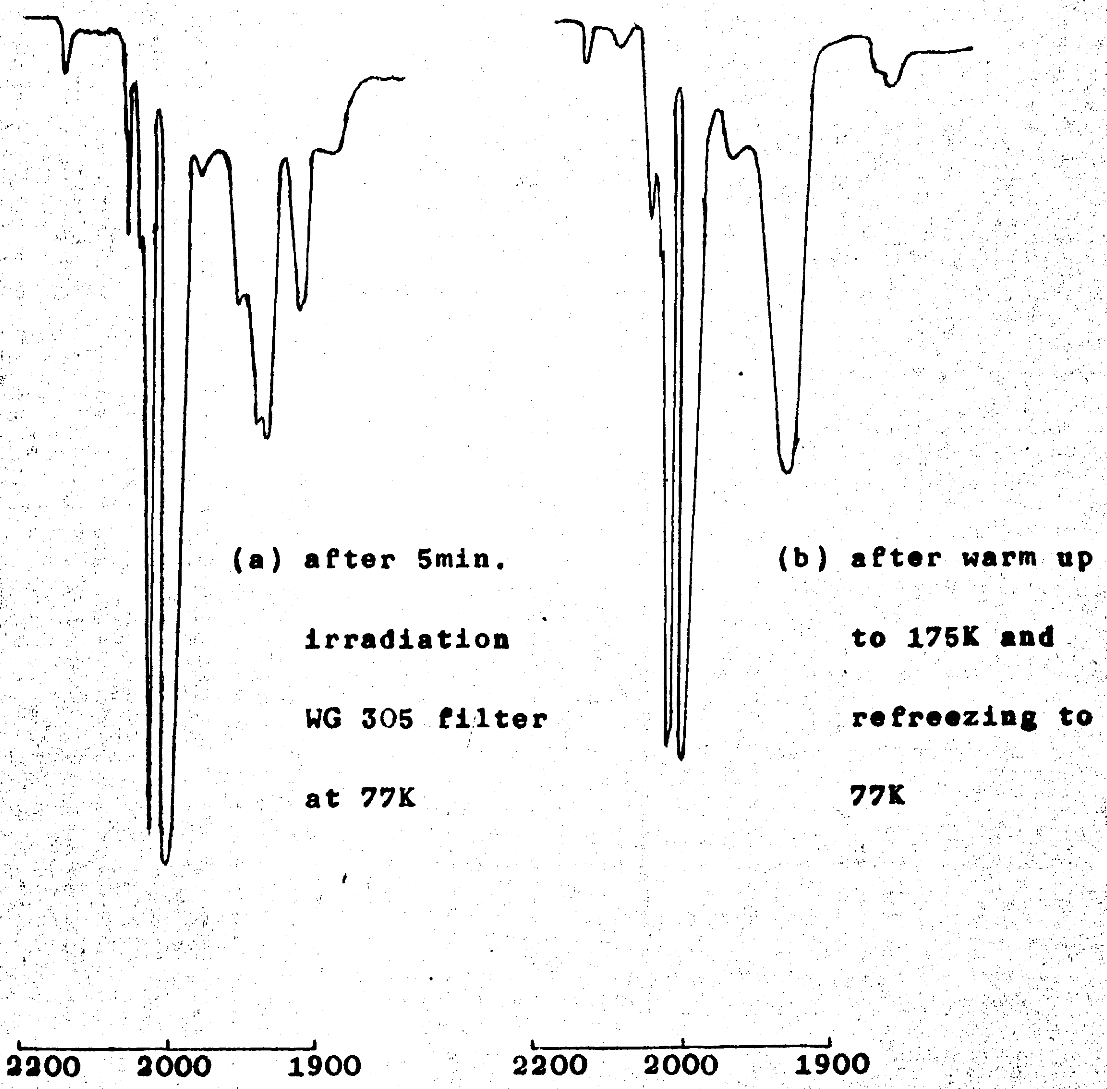


trans isomer is formed in MTHF doped hydrocarbon than in pure MTHF. A possible explanation for this is that, if axial CO is preferentially lost from $Fe(CO)_4(MTHF)$ in photolysis (The preferential loss of trans CO has been suggested in photolysis of $W(CO)_5(NR_3)$.[47]), trans-$Fe(CO)_3(MTHF)$(alkane) could then be formed very quickly and the alkane could be subsequently displaced by MTHF. A large number of experiments in varying compositions of MTHF/mch/ip mixtures would be necessary to test this explanation. With some larger ligands (NEt_3 and $P(i\text{-}C_3H_7)_3$) species which are possibly $LFe(CO)_3$(alkane) are observed and will be discussed later. Incidentally, alkane molecules which would seem to be very poor π acceptors could be considered as substituting into $Fe(CO)_5$ in an equatorial site in $Fe(CO)_4$(alkane), although the C_{2v} configuration may be held here by the matrix.

Further photolysis of $Fe(CO)_3(MTHF)_2$ was not observed although it could take place if longer irradiation times (30 mins.) or higher energy light were used. The molecules $Fe(CO)_2(MTHF)_3$ and $Fe(CO)(MTHF)_4$ would be highly unstable because of the large amount of electron density on the metal. At room temperature $Fe(CO)_5$ solutions in MTHF decompose thermally or photochemically to precipitate $Fe_2(CO)_9$ initially and then disproportionate to give Fe(-II) anions and Fe(II) species.

The behaviour of $Fe(CO)_5$ in 4:1 mch:ip with potential ligands other than MTHF present was also investigated. $Fe(CO)_5$ comcentrations were 10^{-2}M and the ligand concentrations about 1M in these experiments. Freezing of solutions with pyridine,triethylamine, triisopropylphosphine, or hexafluorobenzene present showed similar effects to those observed in MTHF doped glass--- the activation of at least one A_1' mode of $Fe(CO)_5$ and the broadening of the E' band indicating pre-photolysis coordination of a potential ligand. A blank experiment using 1M perfluorohexane in 4:1 mch:ip showed no differences from spectra in pure 4:1 mch:ip. Photolysis experiments were carried out in the triethylamine and triisopropylphosphine (TIP) cases only. In the NEt_3 case six and in the TIP case eight new bands were observed after 5 min. photolysis with WG335 and WG305 filters respectively. After fast warm up to 175K and refreezing to 77K these spectra simplify to three band patterns typical of C_{3v} $LFe(CO)_4$. In the $Fe(CO)_5$/TIP case there is some $Fe_2(CO)_9$ present at this stage (absorptions at 2070 and 1860 cm^{-1} -- see fig. 2-8 and table). In both cases $LFe(CO)_4$ bands can be picked out in the glass before softening indicating that there is pre-photolysis association of $Fe(CO)_5$ and the ligand and subsequent replacement of CO on photolysis as in the MTHF case. The remaining bands in the spectra could correspond to those expected for $L_2Fe(CO)_3$. For instance in the TIP case bands at 2010, 1950, and 1909 cm^{-1} could be due to cis-$L_2Fe(CO)_3$ and a fourth

Figure 2-8: $Fe(CO)_5$+TIP in 4:1 mch:ip glass



(a) after 5min. irradiation WG 305 filter at 77K

(b) after warm up to 175K and refreezing to 77K

Frequencies of observed bands:

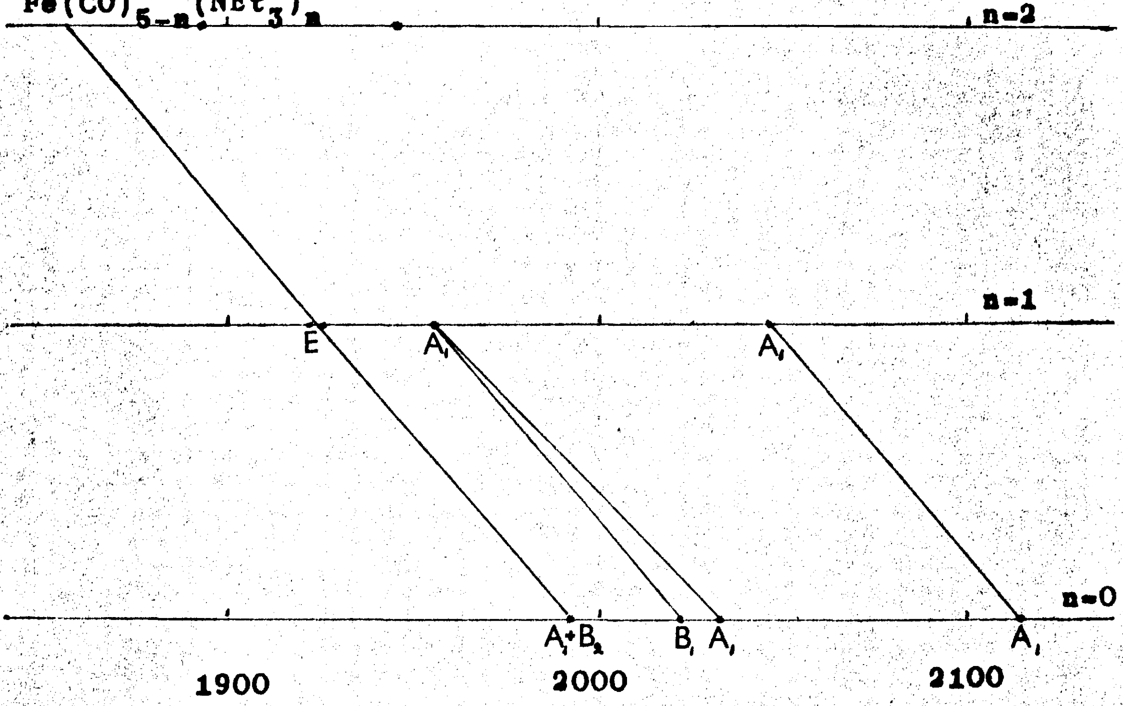
	TIP	NEt_3
$Fe(CO)_4L$	2045	2045
	1965	1954
	1939 1932	1925 1920 1924
Other bands	2010, 1950, 1909, 1882.	1945, 1892.

band at 1882 cm^{-1} to the trans isomer. The E band of $(TIP)Fe(CO)_4$ is split (1939, 1932 cm^{-1}) in a similar way to the E band of $(MTHF)Fe(CO)_4$ and so there is possibly association of phosphine at this stage. However, Boylan[45] photolysed a pure sample of $Fe(CO)_4[P(NMe_2)_3]$ in 4:1 mch:ip glass and observed some splitting of the E band of the starting material on freezing. In the NEt_3 case bands at 2045 and 1954 cm^{-1} persist and the doublet at 1925,1920 cm^{-1} collapses to a single peak at 1924 cm^{-1} on warm up to 175K and refreezing. These bands are assigned to $Fe(CO)_4(NEt_3)$. However, bands at 1945 and 1892 cm^{-1} are at higher frequency than expected for $Fe(CO)_3(NEt_3)_2$. Fig. 2-9 shows Bigorne type correlation diagrams for the $Fe(CO)_5/NEt_3$ and $Fe(CO)_5/TIP$ systems. Again the trans disubstituted species gives a linear correlation in the phosphine case for the E modes, but the other frequencies do not fit the diagram at all. The 1892 and 1924 cm^{-1} bands in the amine case also do not give a linear correlation, but since no such diagrams have previously been constructed for $Fe(CO)_5$/amine systems it is impossible to say what the significance of this is.

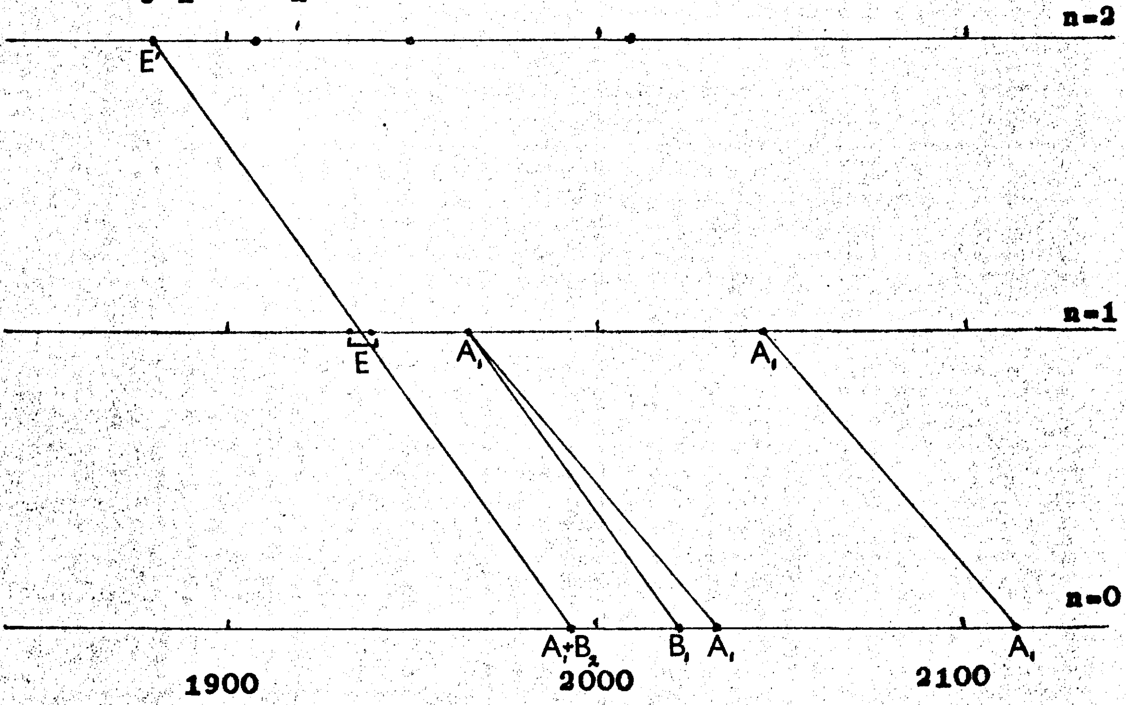
As in the MTHF case association of $Fe(CO)_5$ and potential ligand is important here, but, on the evidence available, the nature of the reactions occurring on irradiation beyond the initial substitution of an axial CO cannot be deduced. A likely possibility is that $Fe(CO)_4L$

Figure 2-9: Correlation diagrams for the $Fe(CO)_5/NEt_3$ and $Fe(CO)_5$/TIP systems.

(a) $Fe(CO)_{5-n}(NEt_3)_n$



(b) $Fe(CO)_{5-n}(TIP)_n$



photolyses to give $Fe(CO)_3L+CO$ and some of the bands observed may be due to $Fe(CO)_3L$. In Boylan's photolysis of $Fe(CO)_4$ $P(p\text{-tolyl})_3$ he observed a primary product with two bands at 2002 and 1921 cm^{-1} in approximately the right intensity ratio for C_{3v} $Fe(CO)_3L$ or $Fe(CO)_3(L)(alkane)$ 45.

Conclusion

The photochemistry of $Fe(CO)_5$ in solution is still far from well understood, but the information in this chapter probably provides the most direct clue to the intermediates involved in such photochemical reactions. In pure hydrocarbon solution the most important intermediate in the formation of polymeric iron carbonyls and CO exchange is probably $Fe(CO)_4(alkane)$. However, when a Lewis base is present, pre-photolysis association of $Fe(CO)_5$ and base may mean that the alkane complex is not important here. Associates of the type $Fe(CO)_5(MTHF)$ are almost certainly present in solutions in donor solvents at room temperature and may also be present in low concentration in hydrocarbon solution. They are probably short lived at room temperature, but, since they have been shown to be much more photoreactive than $Fe(CO)_5$ itself in glass media, could well be important intermediates. The primary reaction in all cases in which a potential ligand is present seems to be loss of one CO from $Fe(CO)_5L$ followed by rearrangement to give $Fe(CO)_4L$.

Secondary photolysis in the presence of a potential ligand probably produces both cis and trans disubstituted products, although further work is required to substantiate this. The axial and equatorial preference of ligands is difficult to explain for MTHF and alkanes, and the rule that worst π acceptors take up axial positions which holds for phosphines and phosphites does not seem applicable. The failure to observe loss of ligands other than CO and the apparent tendency to lose axial CO from $LFe(CO)_4$ are illustrations of two of the concepts discussed in the introductory chapter. The above results could probably be interpreted more meaningfully if the results of detailed kinetic studies on the photoreactions of $Fe(CO)_5$, especially with hard bases, were available.

CHAPTER 3

GROUP VI HEXACARBONYLS

Introduction

The mechanisms of substitution reactions of group VI hexacarbonyls have been studied much more thoroughly than the corresponding mechanisms of $Fe(CO)_5$ reactions.[82,85,86] This is probably because substitution in group VI systems does not usually compete with disproportionation and polymerisation reactions as in the iron case. The mechanism of photochemical substitution is thought to be loss of CO from excited $M(CO)_6$ followed by nucleophilic attack by ligand on $M(CO)_5$[85] while in thermal substitution a similar mechanism involving CO loss as a first step is thought to compete with a second order mechanism involving ligand-hexacarbonyl association as a first step.[86]

There have been several flash photolysis studies of $Cr(CO)_6$ in cyclohexane solution[87-89] and two matrix photolysis studies,[14,25] one in hydrocarbon glass,[14] all of which show a primary photolysis step of $M(CO)_6 \longrightarrow M(CO)_5+CO$. As mentioned in the introductory chapter, the structure of the ground state of $M(CO)_5$ was a subject of controversy,[28] but it has now been shown that this is almost certainly C_{4v} (square pyramidal).[25,26,90] Very recent gas matrix work suggests that the $M(CO)_5$ species observed to date are in fact $M(CO)_5$---S where S is a matrix material weakly interacting with the fragment,[90] but all these $M(CO)_5$---S species are very similar, from their i.r. spectra.

In the course of this work some aspects of the spectra $M(CO)_6$ and $M(CO)_5$ in hydrocarbon and 2-methyltetrahydrofuran (MTHF) glass not previously noted have been examined and the photolysis has been extended to produce $M(CO)_4$ etc. Reactions occurring on glass softening in the presence of unusual ligands have also been examined.

Photolysis in Hydrocarbon Glass

Like $Fe(CO)_5$, group VI hexacarbonyls dissolved in 4:1 mch:ip mixtures show changes in their i.r. spectra on freezing. The T_{1u} band shows a shift of about 3 cm^{-1} to lower frequency in each case, but its shape is not much altered except in high concentrations of hexacarbonyl ($\sim 10^{-1}$M) where there is probably some aggregation taking place. The T_{1u} band frequencies ($Cr(CO)_6$ 1980 cm^{-1}; $Mo(CO)_6$ 1983 cm^{-1}; $W(CO)_6$ 1978 cm^{-1}) in the glass were considerably lower than those observed in Ar matrices at 20K (Cr 1992.0, 1986.6 cm^{-1}; Mo 1997.3,1992.3 cm^{-1}; W 1995.2,1990.0 cm^{-1})[25] and the $Cr(CO)_6$ frequency was less than 1985.4 cm^{-1} observed in a CH_4 matrix.[37] The order of frequencies $Cr(CO)_6 < Mo(CO)_6 > W(CO)_6$ seems to be typical of solutions of hexacarbonyls and has been observed in CCl_4[91] and hexachlorobutadiene[92] solutions as well as hydrocarbon. (The spectra run in hexachlorobutadiene mulls were originally assigned as spectra of solid hexacarbonyls, but more recent work[91] has shown that they were probably in fact solution spectra.) Bands due to $M(CO)_5(^{13}CO)$ become sharper on cooling as expected.

The A_1 band mainly due to ^{13}CO stretch becomes more distinct and shifts to lower frequency (1958 to 1952 cm^{-1} in $Mo(CO)_6$) and another band is observed around 2010 cm^{-1}, probably due to another A_1 mode observed by Bor[93] at 2010.9 cm^{-1} in cyclohexane at room temperature and at 2010.4 by Perutz[90] in methane at 20K for $Mo(CO)_5(^{13}CO)$.

Group VI hexacarbonyls are much less soluble than $Fe(CO)_5$ and so occasionally crystallisation took place during cooling. In most cases where higher concentrations of hexacarbonyl ($>10^{-2}M$) were used a weak band developed around 2020 cm^{-1} and a weak shoulder appeared on the low frequency side of the T_{1u} band of isolated hexacarbonyl (around 1970 cm^{-1}). These effects were assigned to some crystallisation taking place on cooling. Occasionally, for no apparent reason, much more extensive crystallisation took place and the spectra recorded in these cases are probably spectra of solid hexacarbonyl with the spectrum of isolated molecules superimposed (see fig. 3-1). The i.r. spectra of solid group VI hexacarbonyls have been notoriously difficult to obtain[91] because of the high intensity of the T_{1u} absorption. This absorption is split into twelve components, five of which are i.r. active, because of lowering of site symmetry and correlation field splitting in the crystal and the E_g mode, which absorbs at slightly higher frequency, (around 2020 cm^{-1}) is similarly split into eight components, three of which are i.r. active.[94] The result is that the spectrum of solid

$M(CO)_6$ for all three metals in the region around 2000 cm^{-1} consists of eight overlapping bands and appears as a very broad band with three peaks. The presence of small amounts of solid seems to have little effect on photolysis, at least in the initial stages, but leads to polymer formation later.

Photolysis at 77K with WG 305 filtered light gave the expected three band pattern of a C_{4v} metal pentacarbonyl[14,25,26]. Observed frequencies are recorded in table 3-1. A fourth very weak band at 1997 cm^{-1} is observed in the case of $Mo(CO)_5$. This band may be due to equatorially substituted $Mo(CO)_4(^{13}CO)$ —— a corresponding band is observed at 1994.9 cm^{-1} by Perutz —— or more likely is due to some polymeric species such as that observed by Sheline et al.[14] having a band at 1995 cm^{-1}(see later).

Photolysis with higher energy (unfiltered) light led to the formation of two new species. The first formed has four i.r. bands whose frequencies are given in table 3-1. The relative intensity pattern is (at least qualitatively) consistent with that expected for a C_{2v} $M(CO)_4$ fragment. The spectra were simplest in the $Mo(CO)_4$ case where only one band overlapped with a band of another species (see fig. 3-2) and so $Mo(CO)_4$ will be discussed in detail first.

$Mo(CO)_4$ is a fourteen electron fragment and so any tetrahedral form of $Mo(CO)_4$ would have a degenerate ground state and so would be expected to

Table 3-1: Observed frequencies of group VI pentacarbonyls and tetracarbonyls in 4:1 mch:ip glass at 77K. (units cm^{-1})

M		Cr	Mo	W
$M(CO)_5$	A_1	2087	2090	2092
	E	1953	1961	1951
	A_1	1925	1922	1921
$M(CO)_4$	A_1	2055	2052	2056
	B_1	1942	1937	----
	A_1	1913	1921	1919
	B_2	1891	1871	1887 1880

Figure 3-1: $Mo(CO)_6$ in 4:1 mch:ip

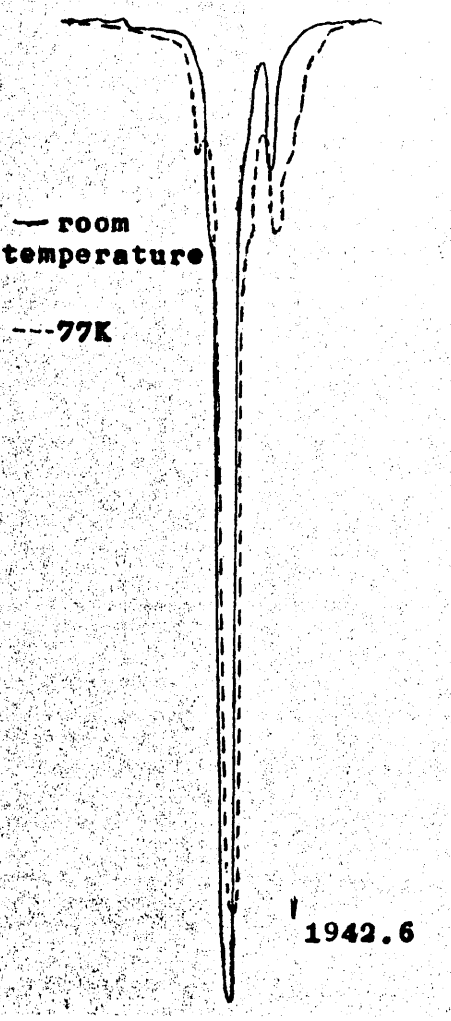
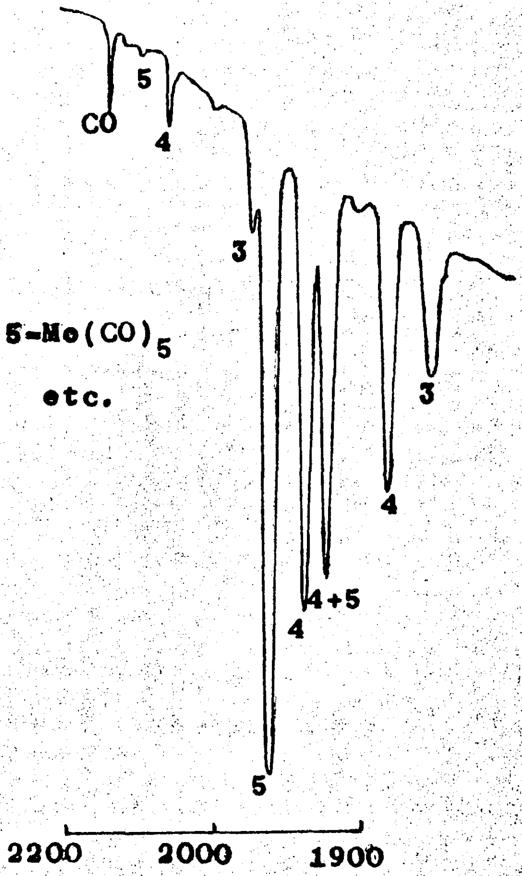


Figure 3-2: $Mo(CO)_6$ in 4:1 mch:ip after 25 min. unfiltered irradiati

at 77K



show Jahn-Teller distortion. A C_{2v} form of $Mo(CO)_4$ could arise in this way, or by loss of two cis CO groups from $Mo(CO)_6$ and retention of octahedral configuration about the metal, i.e. cis-$Mo(CO)_4(vacancy)_2$.

All four bands of $Mo(CO)_4$ are easily observable so in theory $C\hat{M}C$ bond angle calculations based on the relative intensities of the bands are possible[95] if certain assumptions are made:- (1) that the dipole moment derivatives of symmetry related MCO groups are the same under vibrations of different symmetry, and (2) that the degree of mixing of the two A_1 modes can be estimated reasonably accurately from a simplified (CO-factored) force field. In many cases bond angle calculations including assumption (1) are fairly successful, giving angles within 5^o of values obtained from crystal structures e.g. $CpMn(CO)_3$ (see chapter 5), $Mn(CO)_5X$.[97] However, Hyde and Darensbourg[98] calculated dipole moment derivatives for a number of cis $M(CO)_4L_2$ compounds assuming that the angle between trans CO groups was close to 180^o and the angle between cis CO groups was close to 90^o (Values close to these are found in crystal structures[99,100]) and found a value of one dipole moment derivative ($\mu'(A_1^{(2)})$) very much lower than the other three. The explanation proposed for this is that the dipole change during the $A_1^{(2)}$ vibration is perpendicular to the M-C-O bond axis and is of a totally different type to the other dipole changes. A similar explanation has been proposed to explain apparent anomalies in the absolute intensities of bands of $M(CO)_5X$[101]. It is difficult to imagine how a component of dipole moment change perpendicular to the bond axis could arise in C_{2v} $M(CO)_4$ since all the orbitals of both metal and CO are either symmetric or antisymmetric about mirror planes containing M-C-O bond axes.

Assumption (2) was also made in Hyde and Darensbourg's work. It has been shown that the main disadvantage of a CO factored force field is its failure to give reliable values for interaction constants[33]. The degree of mixing of the A_1 modes is given by the relevant elements of the L matrix which relates symmetry coordinates to normal coordinates and these L_{ij} are in turn related to force constants and interaction constants in the following way:—

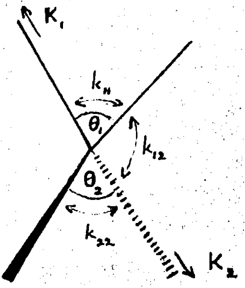
$$\tan 2\phi = \frac{2F_{12}}{F_{11}-F_{22}} \qquad (1)$$

$$L_{11}=L_{22}=\sqrt{G}\cos\phi \qquad (2)$$

$$L_{21}=-L_{12}=\sqrt{G}\sin\phi \qquad (3)$$

where F_{ij} are F matrix elements —— in the case of C_{2v} $M(CO)_4$, $F_{11}=K_1+k_{11}$, $F_{22}=K_2+k_{22}$, and $F_{12}=2k_{12}$ where K_1 and K_2 are CO stretching force constants and k_{11}, k_{22}, and k_{12} are interaction constants as defined in fig. 3-3. G is the reduced mass of CO.

<u>Figure 3-3</u>



Since there are only four CO stretches, only four constants can be determined and so it is necessary to assume some relationship between two of the parameters. In the Cotton-Kraihanzel approach[18] which was developed for substituted hexacarbonyls with a basic octahedral structure the appropriate assumption, based on π bonding theory, is $k_t=2k_c=2k_{c'}$ (here $k_{11}=2k_{12}=2k_{22}$). However, results of calculations on isotopically substituted $Fe(CO)_4I_2$[102], which probably has a value of $\theta_1<180^\circ$, suggest that $k_{11}=k_{22}\neq k_{12}$ would be more appropriate. In a structure close to tetrahedral $k_{11}=k_{12}=k_{22}$ would be approximately true. Force constants were calculated assuming $k_{11}=k_{22}$ (method (a)) and assuming $k_{11}= 2k_{22}$ (method (b)). The results are shown in table 3-3 together with the results of calculations on $Mo(CO)_4$ in a CH_4 matrix where additional data from ^{13}CO substitution studies was used.[90]

Table 3-3

	(a) $k_{11}=k_{22}$	(b) $k_{11}=2k_{22}$	(c) ref. 90
K_1	15.77	15.97	15.941
K_2	14.90	14.69	14.929
k_{11}	0.62	0.82	0.657
k_{22}	0.62	0.41	0.553
k_{12}	0.48	0.41	0.437

Units: md/A

The results of method (a) will be more accurate for an approximately tetrahedral molecule and the results of method (b) more accurate for a cis disubstituted octahedral structure. Van der Kelen et al. used a force field similar to Cotton-Kraihanzel but with $k_t=2k_c \neq 2k_{c'}$ for calculations on $(Mn(CO)_4X)_2$ compounds where the local symmetry about each metal is C_{2v}.[103] However, in this case fortuitously $k_{22}=k_{12}$ i.e. $k_c=k_{c'}$.

Bond angles were calculated using both sets of results including assumption (1) and the results are shown in table 3-4. Only L_{ij} results from method (b) taking the $A_1^{(1)}$ and $A_1^{(2)}$ modes as being out of phase give sensible angles.

Table 3-4

Method (a): $L_{11}=L_{22}=0.315$ $L_{12}=-L_{21}=0.203$

A_1 modes out of phase	$\theta_1=149°$	$\theta_2=52°$
A_1 modes in phase	$\theta_1=75°$	$\theta_2=82°$

Method (b): $L_{11}=L_{22}=0.344$ $L_{12}=-L_{21}=0.168$

A_1 modes out of phase	$\theta_1=173°$	$\theta_2=73°$
A_1 modes in phase	$\theta_1=104°$	$\theta_2=97°$

Relative band intensities were measured for a number of spectra by measuring the peak height and FWHM width of bands. The low frequency A_1 band overlaps with the low frequency A_1 band of $Mo(CO)_5$, but the contribution from $Mo(CO)_5$ to this band could be estimated since the $E:A_1$ ratio for $Mo(CO)_5$ is known and the E band is distinct. However, the calculated angles were fairly insensitive to changes in band intensities, but were much more sensitive to small changes in k_{12}. A change of ± 0.1 md/A in k_{12} produced changes of around ±9° in bond angles.

Recently Perutz and Turner have carried out force field calculations on ^{13}CO substituted $Mo(CO)_4$ in a CH_4 matrix at 20K and calculated bond angles using the results[90]. They have also shown that the out of phase solution can be used to calculate relative band intensities in the spectra of isotopically substituted species which are close to those observed and so the out of phase solution is probably correct. Their values of θ_1= 174.4° and θ_2=107.4° (±5°) in the out of phase solution are likely to be more accurate than those calculated in this work since the force field calculations are more rigorous. They suggest that $Mo(CO)_4$ has a structure based on octahedral so that it is not surprising that method (b) should give better results in this work. Angle calculations using L_{ij} values calculated from Perutz's force constants and intensity ratios from this work gave values of θ_1=168° and θ_2=78° in the out of phase solutio . Again the value of θ_2 is smaller than expected and this may be the result of some structural difference between $Mo(CO)_4$ in glass and $Mo(CO)_4$ in CH_4, and suggests that possibly the species under examination is not $Mo(CO)_4$ but $Mo(CO)_4(alkane)_2$, the alkane having a greater steric requirement than CH_4.

Even the approximate force constants show a general trend $Mo(CO)_6$[25]>$Mo(CO)_5$[25]>$Mo(CO)_4$ which is always found when CO is replaced by a non-π-accepting ligand in metal carbonyl derivatives In this case the 'non-π-accepting ligand' may either be a vacancy or a weakly interacting alkane. Perutz[90] has shown that the visible spectrum of $Cr(CO)_4$ does not change much in different matrices unlike that of $Cr(CO)_5$.,and so presumably there is less interaction between $Cr(CO)_4$ and the matrix material (cf. $Fe(CO)_4$ and $Fe(CO)_3$). $Mo(CO)_4(alkane)_2$ is therefore likely to be a very weak complex.

$Cr(CO)_4$ and $W(CO)_4$ were formed under similar conditions to $Mo(CO)_4$, but their medium frequency bands overlapped considerably with the corresponding pentacarbonyls and tricarbonyls. $Cr(CO)_4$ especially was extremely unstable to photolysis and could only be generated in low concentration. All the tetracarbonyls showed photoreversal to $M(CO)_5$ when irradiated with WG 335 filtered light, but in the $Cr(CO)_4$ case photoreversal was very fast indeed. $Cr(CO)_4$ was never observed in the absence of $Cr(CO)_3$ which is presumably its photolysis product and so the small amount of $Cr(CO)_4$ observed is presumably a steady state concentration.

The next species formed has two i.r. bands at 1972 and 1850 cm^{-1} in the Mo case and is most likely $M(CO)_3$. Table 3-5 lists the observed frequencies for all three metals:---

<u>Table 3-5</u>

	$Cr(CO)_3$	$Mo(CO)_3$	$W(CO)_3$
'A_1'	1975^a	1972^a,1980^b	1967^a
'E'	1858^a	1850^a,1862^b	1847^a

a this work   b ref. 90, methane, 20K   units cm^{-1}

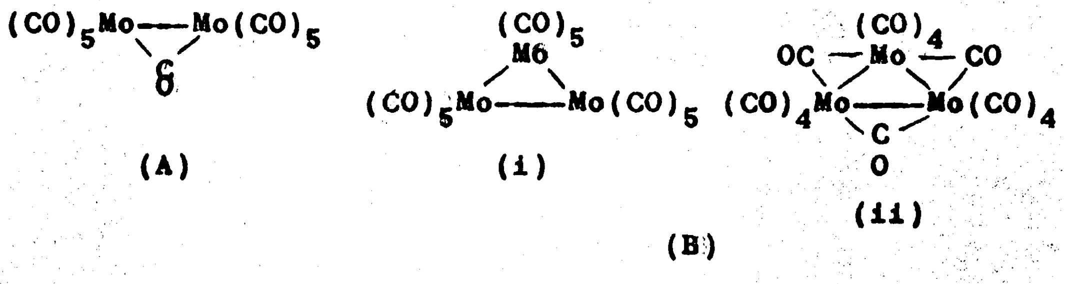
The two bands are in approximately the right intensity ratio for the A_1 and E bands of a C_{3v} tricarbonyl with the higher frequency (A_1) band much sharper than the other. However, isotopic substitution work in methane matrices[90] has shown that $Mo(CO)_3$ is C_{3v} with about 40% of molecules distorted to C_s. The stabilities of all three tricarbonyls seem to be similar. After about 70 min. photolysis of $Mo(CO)_6$ a very weak band was observed at 1909 cm^{-1} which may be due to $Mo(CO)_2$.[90]

In the $Mo(CO)_6$ and $W(CO)_6$ cases several very weak bands apparently unrelated to the bands of the simple photolysis products were observed even after photolysis with WG 305 filtered light. In order to observe these bands relatively high concentrations ($\sim 2 \times 10^{-2}$M) of starting material had to be used; so it is likely that they are due to polymeric species. Their intensities are not reproducible for a particular concentration of starting material which also indicates that they are due to polymeric species the concentration of which will depend on the amount of association of hexacarbonyl in the glass which will depend on the rate of cooling as well as the concentration of the starting solution. The polymeric species are only observed as minor products, so there may be other bands beside those observed.

In the Mo case there are at least two polymeric species formed in the glass: one absorbing at 2108 cm^{-1} and the other at 2081 and 1997 cm^{-1}. On warm up the 2108 cm^{-1} band disappears below 100K, while the other two persist to above 113K and under certain circumstances actually grow as $Mo(CO)_5$ disappears. The 1997 cm^{-1} band is probably the band which Sheline[14] observed at 1995 cm^{-1} and assigned to D_{3h} $Mo(CO)_5$. M.J. Boylan[26] observed two bands similar to Sheline's at 1997 and 2005 cm^{-1} in mch: isooctane glass after softening, but the occurence of these bands was accompanied by production of solid hexacarbonyl; so the 2005 cm^{-1} band which was not observed in this work is probably due to solid. The 2081 cm^{-1} band is much weaker than the 1997 cm^{-1} band and was probably obscured by solvent absorptions in Sheline's and Boylan's spectra. There is a possibility that the 2108 cm^{-1} band is not due to a polymer at all but to CO interacting with a pentacarbonyl in the same way as in a CO containing gas matrix[104]. In the W case a band at 2035 cm^{-1} which appeared after prolonged (70 min.) irradiation is probably due to polymer.

There is very little information in the bands observed about the structure of these polymers. In the Cr case a polymer of the type $Cr_2(CO)_{10 \text{ or } 11}$ including a Cr-C-O-Cr bridge has been suggested because of the similarity of its u.v./visible spectrum to $Cr(CO)_5$ in a CO matrix where the interaction $(CO)_5Cr....CO$ is thought to be important.[104] In the Mo and W cases there is a possibility of polymers including a seven or eight coordinate metal being formed and structures such as (A) and (B) in fig. 3-4 could maintain an eighteen electron configuration about the metal in spite of being CO deficient.

Fig. 3-4



These polymeric species all persist slightly longer than $M(CO)_5$ after glass softening. Absorptions in the 1870-1800 cm^{-1} region due to bridging CO were not observed, but could well have been present since only very low concentrations of polymers were observed.

Reactions Occurring After Glass Softening in Hydrocarbon.

When a matrix containing reactive photolysis products is allowed to soften there are three types of reaction which can occur: (i) recombination to regenerate starting material, (ii) polymerisation of reactive species, and (iii) reaction with impurities. In the case of glasses containing group VI pentacarbonyls and tetracarbonyls all three processes can occur.

Recombination with CO occurs from about 90K upwards in 4:1 mch:ip, but the rate of regeneration of $M(CO)_6$ very quickly slows down. Presumably this is because $M(CO)_5$ fragments with CO close to them, i.e. in the same solvent cage, recombine with it as soon as movement of CO in the glass becomes possible. However, after this type of recombination is complete, the remaining $M(CO)_5$ takes part in other reactions faster than recombination with CO. Since, in almost all cases, starting material is completely regenerated, $M(CO)_6$ must be thermodynamically stable with respect to polymers or impurity complexes and CO, but as extensive regeneration of hexacarbonyl does not normally take place until above 220K, there must be a kinetic barrier to recombination with CO.

Apart from recombination the main reactions in the initial stages of slow warm up result in the formation of polymer of the type described above, but as warm up continued another type of species was formed in almost every case, no matter which metal or what rate of warm up was used. This species (I) had four i.r. bands (two very broad) (fig. 3-5) and a characteristic absorption in the blue region of the visible spectrum causing a yellow colour. It began to form, in solutions containing $M(CO)_5$ only at least, around 113K and disappeared around 230K, being stable for several hours at 195K. Frequencies of i.r. and visible bands are given in table 3-6. Attempts were made to isolate this species at room temperature by carrying out irradiation of a hexacarbonyl containing glass in a flask and pumping off CO as the glass softened. However, in the absence of CO solutions disproportionated to $M(CO)_6$ and metal around 260K and the solid obtained by pumping off solvent at 195K (yellow powder) always contained mainly hexacarbonyl. The yellow colour in this solid persisted until around 40C in air.

Photolysis of hydrocarbon solutions of hexacarbonyls at 195K in a sealed cell produced the same species (I) and so did photolysis

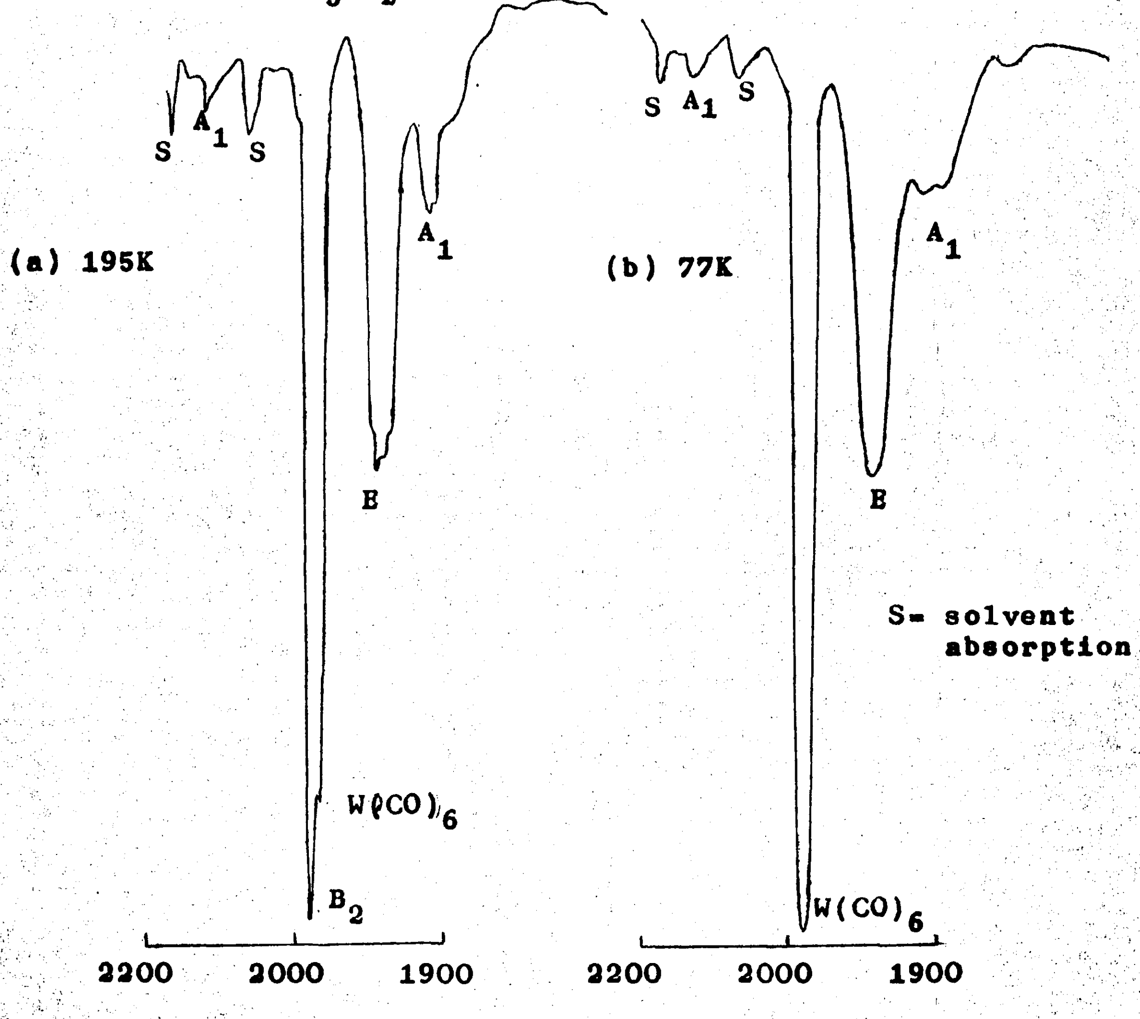
Table 3-6: Observed I.R. and Visible Frequencies for Species (I) at 195K.

M	Cr	Mo	W
A_1	2080	2085	2075
B_2	1975*	1980	1984
E	1936	1945	1938
A_1	1908	1910	1906
λ_{max} (nm)	483	405	416

Units: cm^{-1}

* predicted at 1990 cm^{-1} by Cotton-Kraihanzel force constants

Figure 3-5: $W(CO)_5(H_2O)$ in 4:1 mch:ip, 1.0 mm path length



in methylene chloride solution at 195K (using WG 335 filtered light). The four possibilities for this species are (a) polymer, (b) isocarbonyl, (c) impurity complex, and (d) solvent complex, and the evidence for and against each of these possibilities will be discussed in turn.

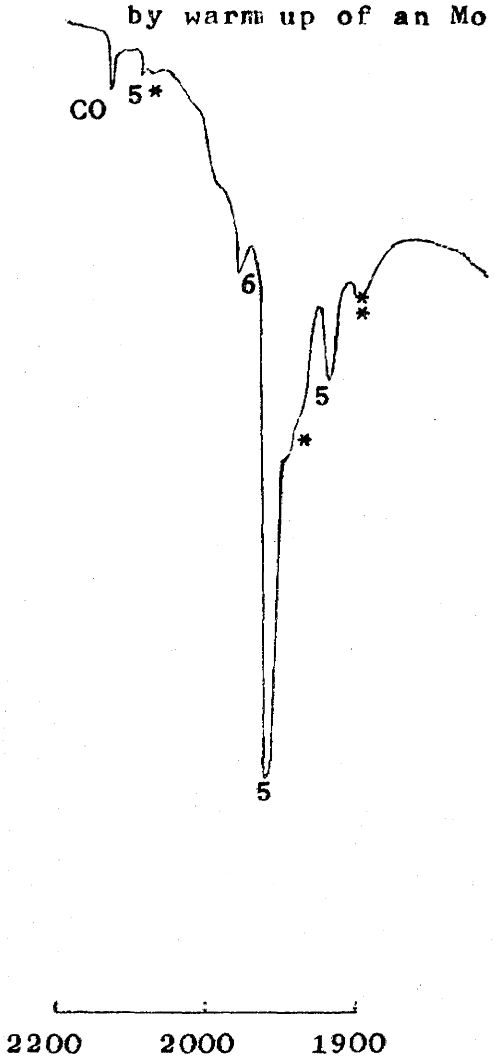
Stable, neutral polymers of group VI carbonyls are not known, but anionic species such as $(HCr_2(CO)_{10})^-$ [105] and $(Cr_2(CO)_{10})^{2-}$ [106] have been characterised. The former type of anion contains a Cr-H-Cr bridge while the latter has a Cr-Cr bond. Since Cr is the smallest of the group VI metals, polymer formation in chromium carbonyls would be expected to be inhibited most by steric factors and this is probably the reason why polymer bands are not observed after photolysis of $Cr(CO)_6$ in glass. The formation of polymeric anions shows that polymerisation of Cr carbonyls is possible, although it may be slow for steric reasons. (I) formed just as quickly for Cr as for the other metals. Paramagnetic $V(CO)_6$, however, does not dimerise, probably for steric reasons.[107]

No i.r. absorption in the region 1700-1500 cm^{-1} could be observed (using a low temperature cell with NaCl inner windows) and so it is unlikely that (I) is a polymer containing a linear M-C-O-M bridge. W-C-O-Al and Mo-C-O-Al bridges are known to absorb in the range 1692-1515 cm^{-1} [108-110]. However, $M(CO)_5$ does not function well as a hard Lewis acid[52] and so it is unlikely that it would behave in the same way as aluminium trialkyls to form stable $M(CO)_5$-C-O-$M(CO)_5$ compounds, although unstable polymers of this type may well form in the glass.[104] The visible absorption maximum of (I) in the Cr case (483 nm) is considerably different from the frequency of $Cr(CO)_5$ in CO matrices (462 nm) which would be thought to have a similar visible spectrum to $(CO)_5Cr{-}C{\leftarrow}O{-}Cr(CO)_5$.

The i.r. bands form a pattern which could be due to a monosubstituted hexacarbonyl although the two lower frequency bands are extremely broad for such a species. The lowest frequency band in particular showed unusual sensitivity to temperature, shifting from 1906 to 1895 cm^{-1} in the W case (fig. 3-5) and becoming considerably broader on cooling from 195K to 77K. The breadth of the two lower bands suggests that they may in fact be composites of a number of bands due to $M(CO)_n$ units in different sites in a polymer. Since there is no band in the 1870-1800 cm^{-1} region, it is unlikely that there are any conventional bridging CO groups present.

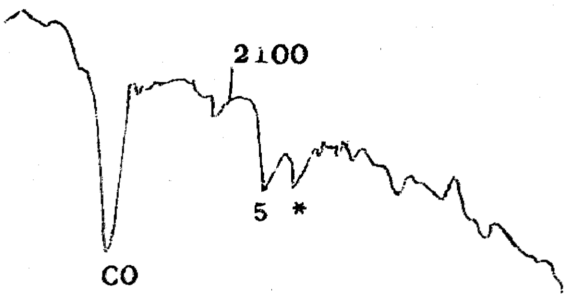
In the Mo case formation of (I) was very much faster when $Mo(CO)_4$ was present in large amounts in the glass and spectra in which $Mo(CO)_5$ and (I) are present at the same time after warming to 92K and refreezing have been recorded (fig. 3-6). However, $Mo(CO)_4$, when present in much lower concentration, persisted until above 100K. It must be noted that the presence of $M(CO)_4$ was not necessary for the eventual production of (I). This relation of the rate of formation of (I) to the concentration of $Mo(CO)_4$ is the strongest piece of evidence for (I) being polymeric, but

Figure 3-6: Spectrum showing $Mo(CO)_5$ and $Mo(CO)_5(H_2O)$ produced by warm up of an $Mo(CO)_4$ containing glass to 92K



6=$Mo(CO)_6$ etc.

*=$Mo(CO)_5(H_2O)$



Region of the above spectrum around 2100 cm^{-1}, scale and ordinate expanded five times.

it is not clear why $Mo(CO)_4$ concentration rather than $Mo(CO)_5$ concentration should affect the rate. Perutz[90] has shown that $Cr(CO)_4$ interacts less strongly with CH_4 than $Cr(CO)_5$ does; so it may be that $Mo(CO)_4$ is less strongly bound to the glass than $Mo(CO)_5$ and so is more reactive towards polymerisation, or possibly (I) is a CO deficient polymer e.g. $M_2(CO)_8$. The last explanation is not likely because the driving force for polymerisation is probably the desire of the metal to attain an eighteen electron configuration.

The possibility of (I) being an isocarbonyl can almost certainly be ruled out as $(CO)_5M....OC$ interactions have been shown to occur when pentacarbonyls are generated in CO matrices and the i.r. and visible spectra in these cases are quite different from those of (I).[104]

The appearance of the i.r. spectrum of (I) at first sight suggests that (I) is a mixture of a number of $M(CO)_5$(impurity) complexes and since it is impossible to make sure that the total concentration of impurities in the system is very much less than the concentration of reactants this explanation seems very likely. However, spectra of (I) were reproducible in different batches of solvent and species which are at least very similar to (I) formed in a variety of solvents --- mch:ip mixtures; n-heptane, methylene chloride, Arcton 113. Co-irradiation of hexacarbonyls with potential ligands, which will be discussed later in this chapter, has shown that when a mixture of monosubstituted compounds is formed, although the E and low frequency A_1 bands usually overlap, the high frequency A_1 bands in the 2100-2075 cm^{-1} region are usually sharp enough to be distinct. (I) shows only one band in this region.

It is still possible that (I) is a complex of some single impurity and so the following possibilities were considered. Since (I) is formed in a variety of solvents, the impurity must be common to them all. The i.r. and visible spectra are similar to those of $M(CO)_5$(ketone) and $M(CO)_5$(alcohol),[111] but it is unlikely that a single ketone or alcohol would be present in all the solvents and no ketonic absorption could be detected in the u.v. spectra of the purified solvents. Impurities which could be present in all the solvents are the atmospheric gases. $M(CO)_5(N_2)$ has been prepared in N_2 matrices, but its spectra are different from those of (I) [38], and attempts to prepare $M(CO)_5(O_2)$ in an oxygen matrix [38] and $M(CO)_5(CO_2)$ in solution (see later) have been unsuccessful. Photoreactions with singlet oxygen are also unlikely at wavelengths of light used. Occasionally in solutions which had been degassed and handled under argon (I) did not form and most of the hexacarbonyl was regenerated by 195K, but this effect was not reproducible and possibly the degassing affects the rate of diffusion of CO through the solution and so allows faster recombination. Another possible impurity is water, which, although it can be removed from the starting solutions, will always be present in the stainless steel parts of the cell and will be very difficult to remove from alumina windows. Monomeric water complexes of group VI carbonyls are not known except for one report of a species isolated from a $Cr(CO)_6$/wet ethanol/KOH mixture which analysed as $K(Cr(CO)_3(H_2O)_2(OH))$.[4] However, when a solution of $(NEt_4)(M(CO)_5Cl)$ (M=Cr,Mo) in water is extracted with 40-60 pet.-ether the i.r. of the pet.-ether layer shows hexacarbonyl and one other band around 1940 cm^{-1} which is presumably the strongest band of $M(CO)_5(H_2O)$. The pet.-ether solution has a faint yellow colour and the coloured species decomposes in a few minutes in air at room temperature.

The spectra of (I) show many of the properties expected of spectra of $M(CO)_5(H_2O)$: the i.r. band positions are close to those expected, the position of the visible band is typical of $M(CO)_5$(hard base) complexes,[112,113] and broadening of the i.r. bands is expected if there is hydrogen bonding between the H_2O ligand and CO groups. However, such hydrogen bonding would be expected to have the greatest effect on equatorial CO groups and would certainly lower the symmetry of $M(CO)_5(H_2O)$ from C_{4v} probably to C_s. This effect would be expected to have a more pronounced influence on the E mode, probably causing it to split, rather than on the A_1 (low frequency) mode which consists mainly of motion of the axial CO group. The A' mode of $M(CO)_5(H_2O)$ which correlates with the B_2 mode in an idealised C_{4v} structure should also be strongly i.r. active, and in $Cr(CO)_5(NH_3)$ the B_2 mode appears moderately intensely at 1977 cm^{-1}.[52] The corresponding mode of $M(CO)_5(H_2O)$ could well be masked by hexacarbonyl. In one spectrum of (I) when very little $Mo(CO)_6$ was present a band was observed at 1980 cm^{-1} which is about 3 cm^{-1} lower than the $Mo(CO)_6$ observed in the same glass earlier in the experiment, , and in another experiment with $W(CO)_6$ as starting material a band is observed at 1984 cm^{-1} overlapping with the $W(CO)_6$ band at 1978 cm^{-1}. Both of these could be the 'B_2' bands of $M(CO)_5(H_2O)$, but they are both relatively sharp compared to other bands of (I). However, B_2 bands of $M(CO)_5$(phosphite) compounds remain fairly sharp while the other bands broaden on cooling (see chapter 4).

Much sharper spectra of (I) were obtained in n-heptane solution using a starting concentration of $\sim 10^{-3}M$ hexacarbonyl and a path length of 1.0 mm. This too can be explained if (I) is $M(CO)_5(H_2O)$ since a lower concentration would reduce the chance of intermolecular hydrogen bonding. Intermolecular hydrogen bonding could also be the reason for the broadening and shifting of the low frequency A_1 band on cooling to 77K if aggregates are formed in which neighbouring molecules are orientated in opposite directions or which have a chain type structure. The bands of $Mo(CO)_5(PH_3)$ show considerable broadening on cooling (see chapter 4).

The main objection to $M(CO)_5(H_2O)$ as the proposed structure for (I) is the relation of the rate of formation of (I), in the Mo case at least, to the concentration of $Mo(CO)_4$. However, since

$Mo(CO)_4$ is probably less strongly bound to the glass than $Mo(CO)_5$.[90] it may be able to form $Mo(CO)_5(H_2O)$ faster if the first step in the reaction is $Mo(CO)_4 + H_2O \longrightarrow Mo(CO)_4(H_2O)$. $Mo(CO)_4(H_2O)_2$ may form, but like $Mo(CO)_4(MTHF)_2$ (see later) it is expected to be much less stable than the corresponding monosubstituted complex. $Mo(CO)_4(H_2O)_2$ has been suggested as a product in the hydrolysis of (7-chloronorbornadiene)$Mo(CO)_4$ in aqueous acetone because the rate depends on the relative concentrations of water and acetone.[114] Attempts to introduce water and D_2O into the glass were unsuccessful as ice precipitated during cooling and no difference in rate of formation of (I) was observed. The band due to $CO...H_2O$ at 2148 cm^{-1} which is observed in Ar matrices[115] was never observed.

The possibility of (I) being a solvent complex is unlikely since the $M(CO)_5$ observed in glass seems to interact like $Fe(CO)_4$ in $Fe(CO)_4$(alkane)[90] and so the solvent complex is present at this stage rather than after glass softening. (I) is obviously something much more stable.

Polymeric species involving OH bridges are known,[116,117] but these are normally produced under fairly forcing conditions, e.g. 16h. reflux in aqueous ethanol with KOH present[116], and contain only three CO groups bound to each metal and, in the case of neutral species, metal hydride bonds. They also show five i.r. bands in different positions from (I).[117] It is therefore unlikely that (I) is such a species although a polymer involving H_2O

cannot be ruled out.

$M(CO)_5(H_2O)$ seems the most likely structure for (I) on i.r. and visible spectroscopic evidence alone. No proton n.m.r. signal other than solvent could be detected in the range $\tau = -2$ to 14 for a solution which was prepared by photolysing $Mo(CO)_6$ in heptane at 195K with WG 335 filtered light and so presumably contained (I), but this was probably due to the low concentration of (I) and so possibly Fourier transform n.m.r. would show a signal. Attempts to concentrate solutions of (I) by pumping off solvent were unsuccessful, causing precipitation of a pale yellow solid which when examined was always mainly hexacarbonyl.

A compound $M(CO)_5(H_2O)$ should be a potential acid — $M(CO)_5OH_2 \rightleftharpoons M(CO)_5OH^- + H^+$ — and the results of generating (I) in the presence of base will be discussed in the section dealing with co-irradiation of $M(CO)_6$ and potential ligands later in this chapter. Attempts to isolate the photolysis products of (I) in glass were also unsuccessful. Even using unfiltered light and irradiation times greater than 60 min. only slow disappearance of starting material was observed; this too could be explained if (I) is $M(CO)_5(H_2O)$ since photolysis, with low energy light at least,[118] is most likely to lead to dissociation of H_2O which will probably be held close to the $M(CO)_5$ fragment by hydrogen bonding and so recombine with it almost immediately. The visible emission spectrum of a species which was almost certainly (I) in the W case has been recorded by Wrighton[119] and shows a maximum at

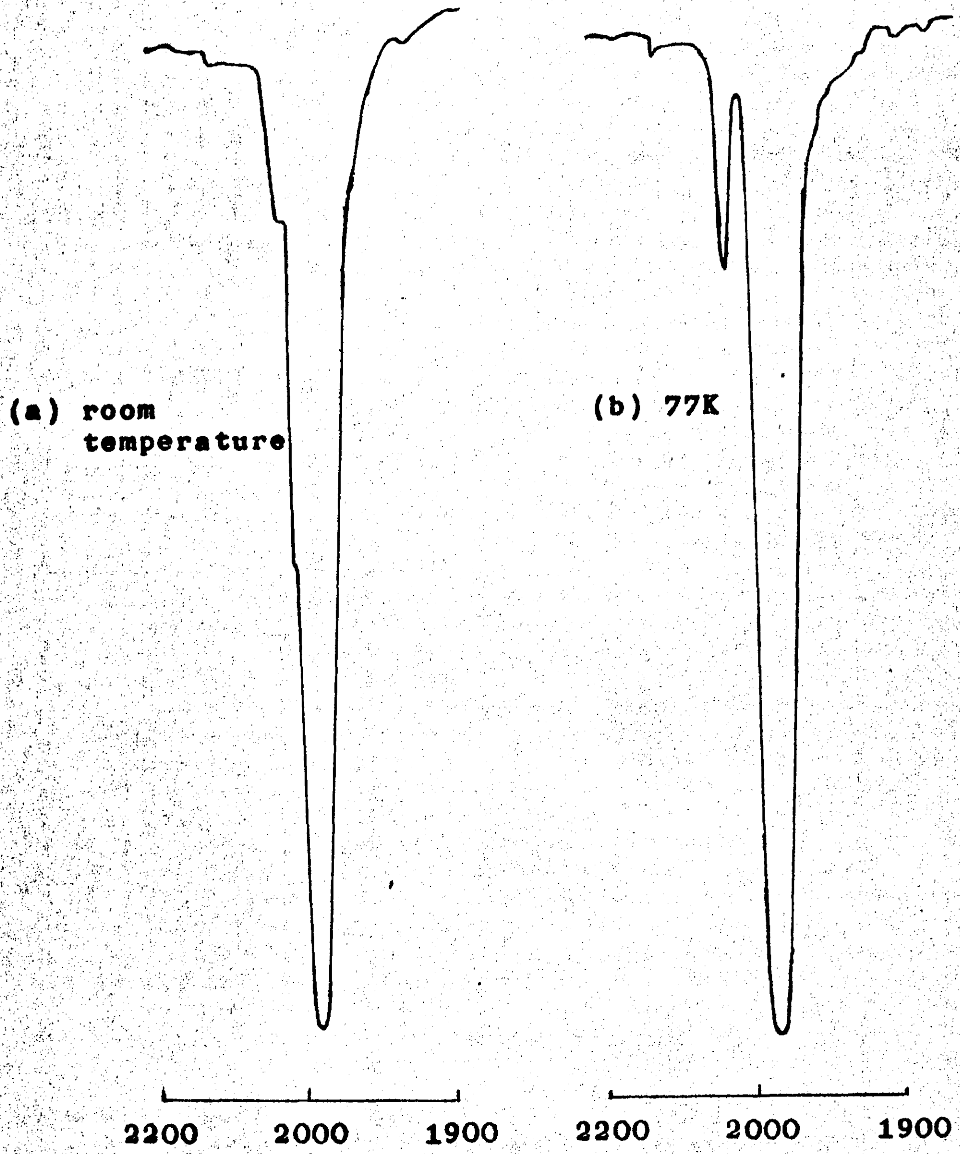
533 nm.

Photolysis in 2-methyltetrahydrofuran Glass

As in the $Fe(CO)_5$ case, spectra of all three hexacarbonyls in MTHF at room temperature were much broader than those in hydrocarbon solution. Shoulders could be observed around 2020 and 2010 cm^{-1} on the high frequency side of the T_{1u} band and the ^{13}CO band at around 1960 cm^{-1} did not resolve. On cooling to 77K the band around 2020 cm^{-1} resolved, but the ^{13}CO band remained hidden and the 2010 cm^{-1} shoulder disappeared completely. A very weak band around 2110 cm^{-1} also became visible (see fig. 3-7 and table). The T_{1u} band shows the same type of incipient splitting as the E' band of $Fe(CO)_5$. These effects can all be explained by the activation of i.r. inactive modes caused by the coordination of MTHF to hexacarbonyl. The band around 2110 cm^{-1} corresponds to the Raman active A_{1g} mode of the hexacarbonyl (2114 cm^{-1} for $Cr(CO)_6$ in CH_2Cl_2 at room temperature[120]) while the band around 2020 cm^{-1} corresponds to the E_g mode (2017 cm^{-1} for $Cr(CO)_6$[120]). Similar effects were observed for $Mo(CO)_6$ in 4:1 mch:ip doped with MTHF, but in that case the ^{13}CO band at 1958 cm^{-1} is resolved at room temperature.

The frequency of the centre of the 'T_{1u}' band shifts on cooling (e.g. $Mo(CO)_6$ 1980 to 1972 cm^{-1}) and the half width increases to about 1.5 times its original value although the width of the band close to the base line does not increase. This is the incipient splitting referred to above. The disappearance of

Figure 3-7: $Cr(CO)_6$ in MTHF



the 2010 cm^{-1} shoulder and the failure of the A_1 ^{13}CO band around 1955 cm^{-1} to resolve at low temperature seem unusual at first sight. However, these effects can be explained if the 2010 cm^{-1} shoulder is due to $Mo(CO)_5(^{13}CO)$ — Bor observed an A_1 mode of $Mo(CO)_5(^{13}CO)$ at 2012 cm^{-1} in hexane.[121] If there is coordination of MTHF to hexacarbonyl in one specific site, two types of $M(CO)_5(^{13}CO)(MTHF)$ if the MTHF is bonded to the metal or more than one CO group, or three types if MTHF is attached to a single CO, are possible. The effect of the presence of these two or three closely related species would be to broaden or split the $M(CO)_5(^{13}CO)$ bands, and this is probably what occurs. In doped hydrocarbon the $Mo(CO)_5(^{13}CO)$ band at 1957 cm^{-1} is sharp and resolved at room temperature, but appears only as a broad shoulder on the T_{1u} band of $Mo(CO)_6$ at 77K. The δM-C-O region of the spectrum was not investigated, but it seems likely that the same type of pre-photolysis coordination of MTHF to a saturated carbonyl which took place in the $Fe(CO)_5$ case is also taking place here.

As expected photolysis in MTHF or MTHF doped hydrocarbon is much faster than photolysis in pure hydrocarbon glass. Primary photolysis in pure MTHF glass gave the expected three bands of a C_{4v} monosubstituted hexacarbonyl. Table 3-9 shows i.r. and visible frequencies for the $M(CO)_5(MTHF)$ species observed. The B_2 mode which is expected to be weakly i.r. active since it is observed in $V(CO)_5(MTHF)^-$ [41] is predicted at 1985 cm^{-1} in the

Table 3-7: Observed frequencies of $M(CO)_{6-n}(MTHF)_n$ in MTHF glass at 77K.

	M	Cr	Mo	W
n=0	'A_{1g}'	2112(w)	2110(w)	——
	'E_g'	2017(m)	2020(m)	——
	'T_{1u}'	1970(vs)	1972(vs)	——
n=1	A_1	2078(w)	2078(w)	2074(w)
	B_2	1983(w)	1985(w)	1980(w)
	E	1933(vs)	1936(vs)	1924(vs)
	A_1	1881(s)	1882(s)	1878(s)
n=2	A_1	2016(m)	2018(m)	2015(m)
	B_1	----*	1884(vs)	1871(vs)
	A_1	1870(sh)	1868(s)	1861(sh)
	B_2	1825(s)	1823(s)	1820(s)
n=3	A_1	1917(m)	1913(m)	1905(m)
	E	1764(vs)	1767(vs)	1758(vs)

* always masked by $Cr(CO)_5(MTHF)$ low frequency A_1 band

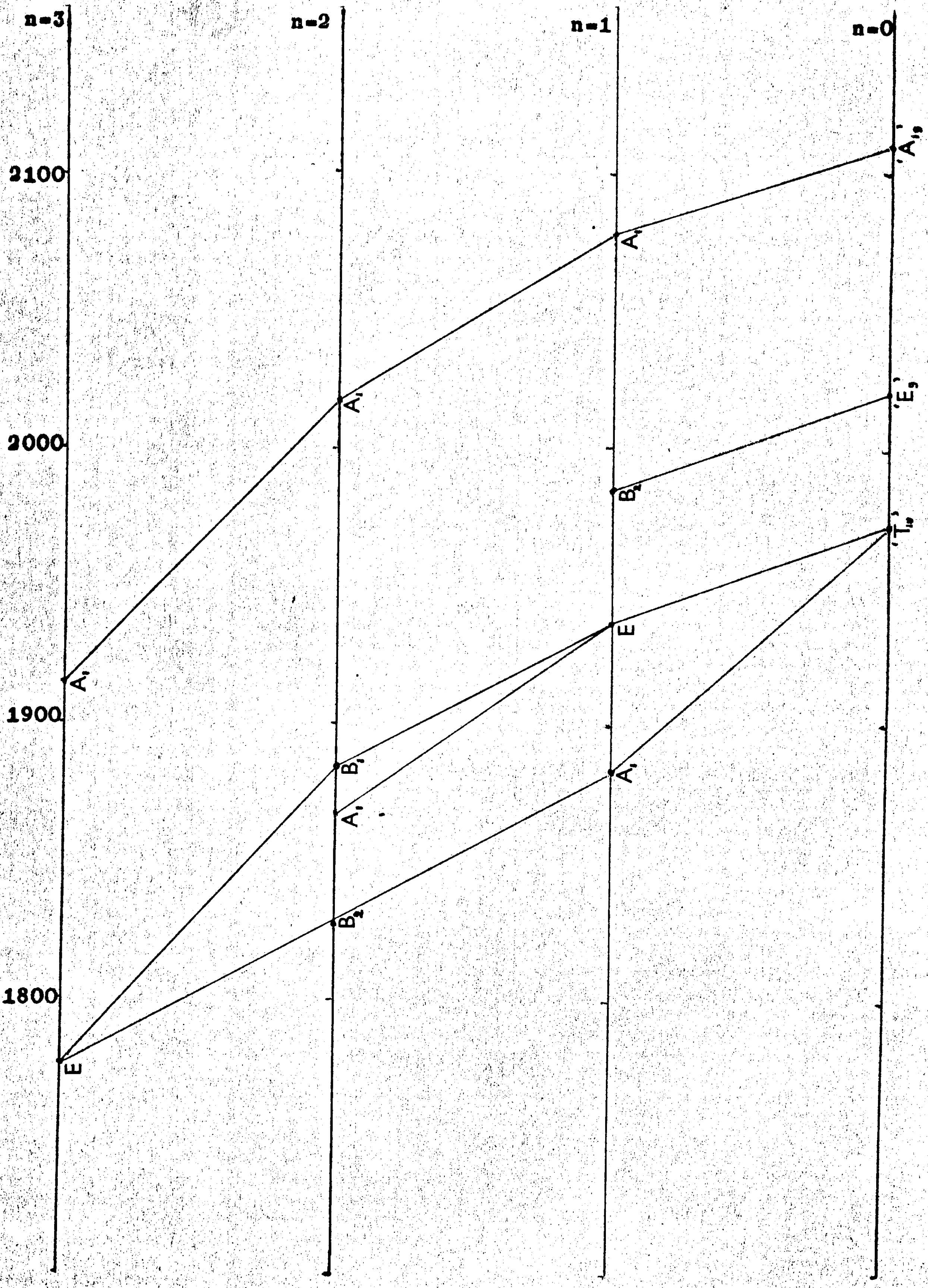
case of $Cr(CO)_5(MTHF)$ using Cotton-Kraihanzel force constants and is observed at 1983 cm^{-1}. B_2 bands are also observed close to the predicted frequencies in the other two cases (see table 3-7). In the Mo and W cases $M(CO)_5(MTHF)$ could be generated without much secondary photolysis and u.v./visible spectra have been recorded (by M.J. Boylan). However, in the Cr case under the same irradiation conditions (30 min. at 77K with a WG 305 filter) secondary and tertiary photolysis was occurring to a considerable extent. Like $Fe(CO)_4(MTHF)$, $M(CO)_5(MTHF)$ compounds all persisted for about 1h. in sealed cells with CO present at room temperature. However, attempts to isolate $Mo(CO)_5(MTHF)$ solid were unsuccessful as this compound seems to disproportionate to $Mo(CO)_6$ and Mo metal in concentrated solution even at 195K. $Fe(CO)_4(THF)$ probably shows a similar instability in the absence of CO since Cotton and Troup[70] found that spectra of $Fe_2(CO)_9$/THF mixtures were extremely complicated if CO atmospheres were not used.

Further photolysis with both unfiltered and WG 305 filtered light led to production of at least two more species. The first of these, most likely $M(CO)_4(MTHF)_2$, showed four i.r. bands with an intensity pattern similar to that expected for a cis disubstituted hexacarbonyl with the B_1 and A_1 (medium frequency) bands overlapping. Unfortunately these bands also overlap with the low frequency A_1 band of $M(CO)_5(MTHF)$; so it is impossible to tell if there is yet a third band in this region due to trans $M(CO)_4(MTHF)_2$, the E_u mode of which is predicted in this region by a correlation diagram (fig. 3-8). The next formed species has two bands, the sharper at higher frequency, typical of a C_{3v} tricarbonyl, and is most likely $M(CO)_3(MTHF)_3$ analogous to the $M(CO)_3$(diglyme) complexes proposed as intermediates in thermal substitutions of hexacarbonyls in diglyme at around 150C.[122] $Mo(CO)_3$(diglyme) is an isolable complex[122], but $Mo(CO)_3(MTHF)_3$ was quickly reconverted to $Mo(CO)_5(MTHF)$ and $Mo(CO)_6$ on allowing the glass to warm up. However, $M(CO)_3(MTHF)_3$ compounds in the glass were all very photostable and neither photoreversal nor farther photolysis products were observed. The frequencies of the bands of $M(CO)_4(MTHF)_2$ and $M(CO)_3(MTHF)_3$ are given in table 3-7.

Fig. 3-8 is a correlation diagram for the system $Mo(CO)_{6-n}(MTHF)_n$. As in the $Fe(CO)_{5-n}(MTHF)_n$ diagram it does not show the near linear correlation found by Bigorne[82] for $Mo(CO)_{6-n}L_n$ where L is a phosphine or phosphite, but a similar type of pattern to correlation diagrams for hard base substituted derivatives e.g. $Mo(CO)_{6-n}(PhCN)_n$[123-4]. An interesting feature of this diagram is the almost linear correlation of the low frequency A_1 mode of $Mo(CO)_5(MTHF)$ with the B_2 mode of $Mo(CO)_4(MTHF)_2$ and the E mode of $Mo(CO)_3(MTHF)_3$. This may well be fortuitous, but these modes all involve stretching of CO groups trans to MTHF.

In hydrocarbon glass 1M in MTHF there is also considerable pre-photolytic association of hexacarbonyl and MTHF. Besides the effects on the spectrum previously described, it was also possible to isolate much higher concentrations of $Mo(CO)_6$ (up to $\sim 5 \times 10^{-2}$M)

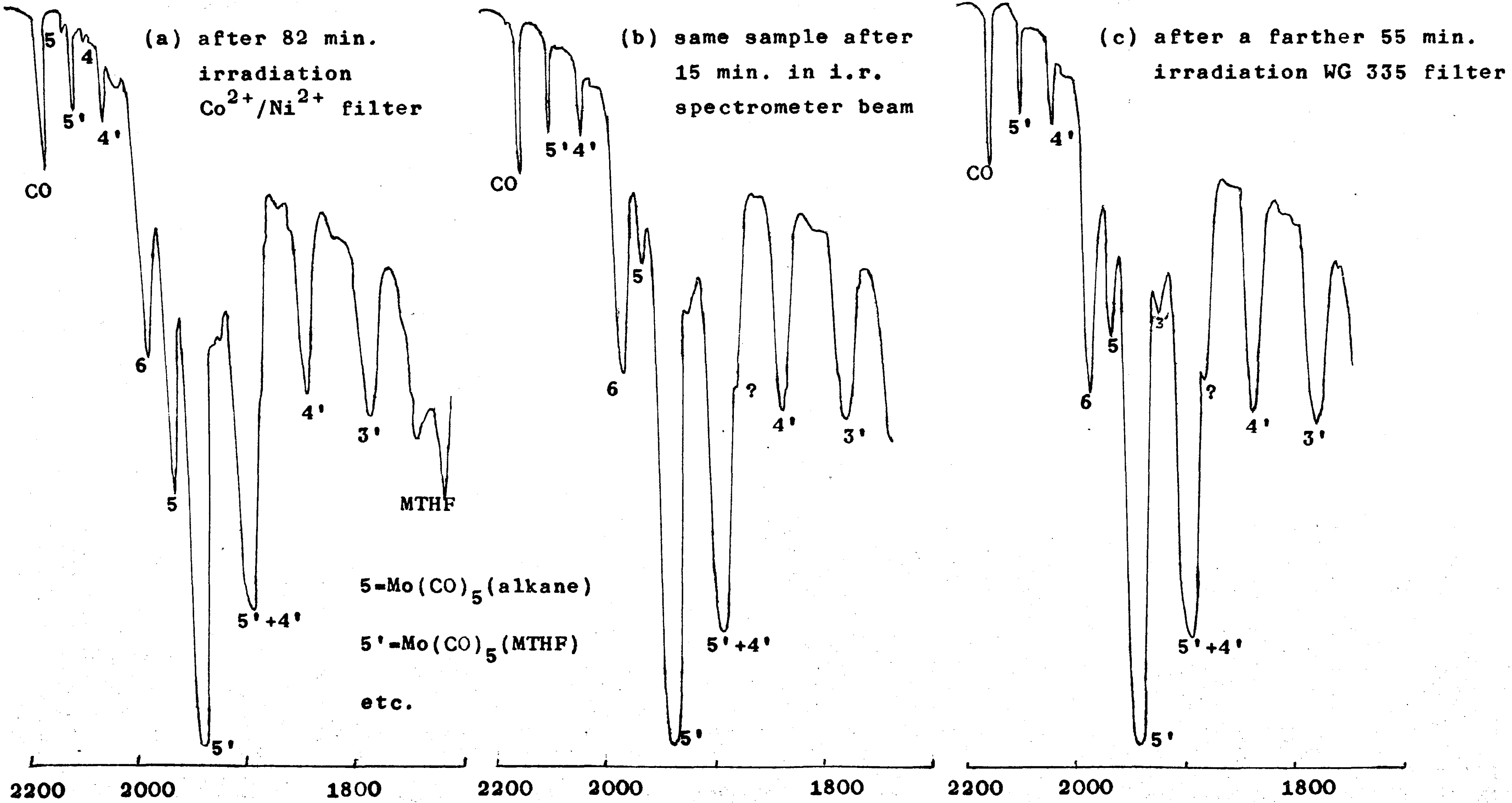
Figure 3-8: Correlation diagram for $Mo(CO)_{6-n}(MTHF)_n$ in MTHF glass at 77K.



when MTHF was present, presumably because (MTHF)Mo$(CO)_6$ is formed before Mo$(CO)_6$ crystallisation takes place. Photolysis at 77K with unfiltered light or a Co^{2+}/Ni^{2+} filter led to production of all Mo$(CO)_{6-n}$$(MTHF)_n$ (n=1,2,3) species with bands which were sharper but in similar positions to those observed in pure MTHF, and four new bands at 2095(w), 1961(s), 1913(m), and 1859(w). These bands all disappear if the sample is allowed to stand in the i.r. spectrometer beam and at the same time a shoulder at 1875 cm^{-1} on a band due to the low frequency A_1 band of Mo$(CO)_5$(MTHF overlapping with the B_1 and $A_1^{(1)}$ bands of Mo$(CO)_4$$(MTHF)_2$ gains intensity and resolves. These effects are due to photolysis in the spectrometer beam and can be stopped by placing a KRS 5 (Tl_2BrI) filter, which absorbs most of the visible light in the beam,between the source and the sample. KRS 5, however, reflects about 25% of the incident i.r., and so spectra obtained using this filter were of very poor quality (similar to those recorded using a germanium filter in an effort to see Fe$(CO)_4$ p. 29). As this photolysis takes place all the bands due to Mo$(CO)_{6-n}$$(MTHF)_n$ grow slightly; so presumably the species responsible for the new bands are being converted to MTHF complexes and undergoing photoreversal to Mo$(CO)_6$, and photolysis of the MTHF complexes is also taking place slowly in the beam.

The three bands at 2095, 1961, and 1913 cm^{-1} form a pattern similar to the three bands of Mo$(CO)_5$ in 4:1 mch:ip (2093(w), 1960(s), and 1922(m) cm^{-1}). This together with the photoreversal

Figure 3-9: $Mo(CO)_6$ irradiated in 4:1 mch:ip 1M in MTHF at 77K



(a) after 82 min. irradiation Co^{2+}/Ni^{2+} filter

(b) same sample after 15 min. in i.r. spectrometer beam

(c) after a farther 55 min. irradiation WG 335 filter

5=$Mo(CO)_5$(alkane)

5'=$Mo(CO)_5$(MTHF)

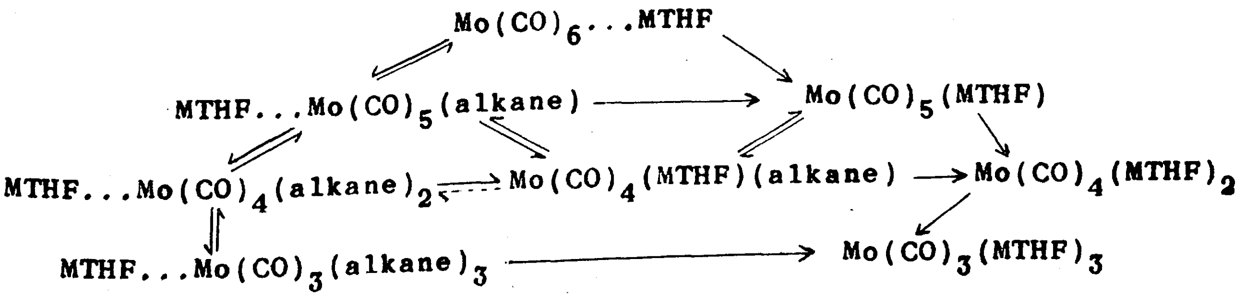
etc.

Co^{2+}/Ni^{2+} solution filter shows a very weak band at 2055 cm^{-1} which also disappears on photolysis in the spectrometer beam and is probably the highest frequency band of $Mo(CO)_4$....MTHF (or $Mo(CO)_4(alkane)_2(MTHF)$).

Irradiation of a sample of $Mo(CO)_6$ in an MTHF/4:1 mch:ip glass which had first been photolysed with Co^{2+}/Ni^{2+} filtered light and then in the spectrometer beam (see fig. 3-9(a)) with WG 335 filtered light led to an increase in the bands due to $Mo(CO)_6(MTHF)$ and $Mo(CO)_5(alkane)(MTHF)$ and the band at 1875 cm^{-1} which appeared as a weak shoulder during photolysis in the spectrometer beam (fig. 3-9(c)), while the band at 1917 cm^{-1} due to $Mo(CO)_3(MTHF)_3$ becomes more clearly separated from the 1937 cm^{-1} band of $Mo(CO)_5(MTHF)$. However, no decrease in $Mo(CO)_5(MTHF)$ bands could be detected —— only the band at 2088 cm^{-1} could provide a reliable guide to the concentration of $Mo(CO)_5(MTHF)$ in these spectra since the E band at 1937 cm^{-1} is so intense that small changes in concentration will not affect it much and the low frequency A_1 band overlaps with two bands of cis-$Mo(CO)_4(MTHF)_2$. Direct photoreversal of $Mo(CO)_5(MTHF)$ to $Mo(CO)_6(MTHF)$ is unlikely, and there does not seem to be enough '$Mo(CO)_4$' present to account for the increase in $Mo(CO)_6(MTHF)$ and $Mo(CO)_5(alkane)(MTHF)$. $Mo(CO)_4(MTHF)(alkane)$, however, could well be present, having been produced by photolysis of $Mo(CO)_5(MTHF)$ or replacement of alkane by MTHF in $Mo(CO)_4(alkane)_2$ in the spectrometer beam. By analogy with $Mo(CO)_4(PR_3)$, which will be discussed in a later chapter, $Mo(CO)_4(MTHF)(alkane)$ is expected to be predominantly cis with four i.r. bands, one around 2020 cm^{-1} and three in the range 1930 to 1870 cm^{-1}. It is therefore possible that this species may be present and that all its bands are masked by $Mo(CO)_5(MTHF)$ and $Mo(CO)_4(MTHF)$, except perhaps a band around 1920 cm^{-1} (see fig. 3-9(a) and (b)). A photoreversal process involving loss of MTHF from $Mo(CO)_4(MTHF)(alkane)$ could lead to regeneration of $Mo(CO)_5(alkane)$ and hence $Mo(CO)_6$.

The band at 1875 cm^{-1} is around the frequency expected for trans $Mo(CO)_4(MTHF)_2$ which could possibly be formed by long wavelength photolysis of $Mo(CO)_5(MTHF)$ if the CO trans to MTHF is preferentially lost, or by photorearrangement of cis-$Mo(CO)_4(MTHF)_2$ involving Mo-C or Mo-O bond breaking and remaking.

The photolysis of $Mo(CO)_6$ in MTHF/hydrocarbon mixtures is extremely complicated, but it would seem from the above evidence that alkane competes with MTHF for CO deficient fragments at every stage and that at least one photoreversal step involving loss of MTHF is involved. The reactions described above are summarised in the following scheme:



Many more experiments including photolysis in hydrocarbon/MTHF mixtures of varying compositions and photolysis of $Mo(CO)_5(MTHF)$

in the absence of CO and excess MTHF are necessary before the system can be fully understood. Photolysis of pure $Mo(CO)_5(MTHF)$ will be very difficult since the compound disproportionates easily to $Mo(CO)_6$, Mo, CO, and MTHF at 0^oC. Since substitution of up to three carbonyls with MTHF was observed, there must be association of more than one MTHF molecule with at least some of the $Mo(CO)_6$ molecules in the glass. However, it seems that one MTHF is coordinated more closely than the others. The band of MTHF between 1700 and 1750 cm^{-1} splits in hydrocarbon glass, but remains unchanged during photolysis, which probably indicates that MTHF forms aggregates in the glass. The above results contrast with the $Fe(CO)_5$ case where $Fe(CO)_4$(alkane) was only observed in glasses containing much less ($\sim 10^{-1}M$) MTHF, and so are consistent with the view that $M(CO)_5$ fragments (M=Cr,Mo,W) are more reactive than $Fe(CO)_4$[90] since $Mo(CO)_5$ reacts with alkane even in the presence of a large excess of MTHF. They also support the idea that photoreversal is in fact an electronic process since photoreversal steps involve loss of alkane or possibly MTHF as well as recombination with CO.

Photolysis in the Presence of Other Potential Ligands

Hexacarbonyls were photolysed in hydrocarbon glass at 77K and in solution at 195K and room temperature in the presence of a number of potential ligands, both basic and non-basic. These reactions were all carried out in situ in sealed i.r. cells, and only in a few cases were they studied as closely as the reaction with MTHF.

(A) Basic Ligands

The selection of ligands used here include acetone, acetaldehyde, cyclohexanone, n-pentanol, THF, NEt_3, PEt_3, PPh_3, $P(i\text{-}C_3H_7)_3$, $P(C_6H_{11})_3$, and $P(OMe)_3$, although the phosphines and $P(OMe)_3$ have some π acceptor properties as well as behaving as σ donors. The ligands will be further divided into sub-sections.

(i) Ketones: The most thoroughly studied reaction of a ketonic ligand was that of $Mo(CO)_6$ with acetone, in which irradiations of $Mo(CO)_6$ in the presence of an excess of acetone (concentrations unknown) were carried out at 77K, 195K, and room temperature. Cooling $Mo(CO)_6$/acetone solutions in 4:1 mch:ip to 77K resulted in slight activation of the $Mo(CO)_6$ E_g mode (2022 cm^{-1}), but no change in the ^{13}CO band except the shift from 1958 to 1953 cm^{-1} which is apparent even in pure hydrocarbon. Photolysis was at a similar rate (at least with pyrex filtered light) to that observed in pure hydrocarbon and the principal product was $Mo(CO)_5$(alkane), although a weak fairly broad band at 1937 cm^{-1} was observed in the early stages of photolysis. This band did not grow much during photolysis and was obscured by $Mo(CO)_4$ in the later stages. All these observations are consistent with a few of the $Mo(CO)_6$ molecules being coordinated to acetone before photolysis and the new band being $Mo(CO)_5$(acetone). During warm up a very broad band around 2010 cm^{-1} appeared around 150K and had disappeared again by 195K, but three bands at 2080, 1940, and

1902 cm^{-1} which appeared at about the same temperature persisted until around 225K, but had disappeared by room temperature when almost all the hexacarbonyl had been regenerated. The three more persistent bands are very similar to the bands of (I) observed in the absence of acetone and are probably due to $Mo(CO)_5(H_2O)$ or possibly $Mo(CO)_5$(acetone) and the broad band at 2010 cm^{-1} is probably due to solid hexacarbonyl. Irradiation of a similar solution at 195K with pyrex filtered light led to the formation of three bands similar to (I) together with three new bands at 2015, 1873, and 1827 cm^{-1}. On fast warm up to room temperature (in <5 min.) most of the hexacarbonyl was regenerated, but a band at about 1940 cm^{-1} persisted for about 30 min. Irradiation in hydrocarbon solution at room temperature showed no change in the $Mo(CO)_6$ band, but irradiation in pure acetone produced bands at 2080(vw), 2065(w), 1942(sh), 1923(s), and 1854(m) cm^{-1}. A literature report of $W(CO)_5$(acetone) in acetone solution[111] describes bands at 2067(w), 1920(s), and 1847(m) cm^{-1}. 1847 cm^{-1} seems an extremely low frequency for a band of a monosubstituted hexacarbonyl and this band is possibly due to cis-$W(CO)_4(\text{acetone})_2$, the other bands of which could contribute to the 1920 cm^{-1} band and be masked by the hexacarbonyl band since bands in pure acetone are very broad. 1920 cm^{-1} is also very low for the E band of $W(CO)_5$(acetone) and this band is possibly a composite of the low frequency A_1 band of $W(CO)_5$(acetone) and the two medium frequency bands of cis-$W(CO)_4(\text{acetone})_2$ and possibly the E_u band of trans-$W(CO)_4(acetone)_2$. Spectra of acetone complexes in acetone solution are thus rather confused and unhelpful in assigning spectra in acetone/hydrocarbon mixtures. $Mo(CO)_5(acetone)$ has probably a CO stretching spectrum similar to $Mo(CO)_5(H_2O)$ with broadening of the bands due to mixing with the acetone C=O stretch at 1720 cm^{-1}. Incidentally no change in this band was observed during irradiation, possibly because a large excess of acetone was used. The band which persists for about 30 min. at room temperature at 1940 cm^{-1} is probably the E band of $Mo(CO)_5(acetone)$. An explanation for the spectra observed on irradiation at 195K is that both $Mo(CO)_5(acetone)$ and $Mo(CO)_5(H_2O)$ are produced and the $Mo(CO)_5(acetone)$ which is the major product photolyses farther to give cis-$Mo(CO)_4(acetone)_2$ and $Mo(CO)_3(acetone)_3$ which are responsible for the bands at 2015, 1873, and 1823 cm^{-1}, the other bands being masked by $Mo(CO)_5(H_2O)$ or $Mo(CO)_5(acetone)$. $Mo(CO)_5(H_2O)$ does not normally form at 195K on irradiation with pyrex filtered light, but acetone has a strong absorption in the near u.v. at 276 nm which means that with the concentrations of acetone used acetone was acting as an internal filter cutting out most radiation $\lambda<320$ nm, and $Mo(CO)_5(H_2O)$ is stable to irradiation at wavelengths longer than this.

It has been shown in room temperature flash photolysis studies that $Cr(CO)_5$ in cyclohexane reacts faster with π donor ligands than with pure σ donors[125]. Acetone could well function as a π

donor by 'sideways' bonding, but such π complexes would be expected to rearrange to less crowded σ bonded structures; so it is probably the case that $Mo(CO)_5$(acetone) forms in preference to $Mo(CO)_5(H_2O)$. However, since the spectra of the two species are probably very similar it is impossible to say that both are not formed. Visible spectra were not examined. Similar results at 195K were obtained for the $Mo(CO)_6$/acetaldehyde and $W(CO)_6$/cyclohexanone systems.

(ii) n-Pentanol: Irradiation of $W(CO)_6$ in the presence of excess n-pentanol in isopentane at room temperature with pyrex filtered light produced three new bands at 2075(vw),1930(m), and 1903(w) which are probably the bands of $W(CO)_5$(pentanol). On prolonged irradiation (>3h) in a sealed cell a steady state concentration of this species was attained.

(iii) Ethers: $Mo(CO)_6$ was irradiated at 195K in the presence of 0.1M THF and in the presence of excess 1,2-dimethoxyethane (glyme) in 4:1 mch:ip using WG 335 filtered light. In the THF case, where the starting concentration of $Mo(CO)_6$ was around 10^{-2}M, the product had three i.r. bands at 2075, 1940, and 1909 cm^{-1}. These are more similar in position and form to $Mo(CO)_5(H_2O)$ than $Mo(CO)_5$(MTHF). On freezing to 77K the bands show the expected broadening for $Mo(CO)_5(H_2O)$ bands, but the 1909 cm^{-1} band shifts to around 1870 cm^{-1} (about 20 cm^{-1} lower than the corresponding band of $Mo(CO)_5(H_2O)$ in the absence of THF). The $Mo(CO)_6$ band also shifts from 1983 to 1980 cm^{-1} and becomes broader on freezing.

On warm up to room temperature almost all the $Mo(CO)_6$ is regenerated. These observations are all consistent with the formation of $Mo(CO)_5(H_2O)$ on photolysis rather than $Mo(CO)_5(THF)$. The spectrum of $Mo(CO)_6$ before photolysis shows no sign of THF ...$Mo(CO)_6$ association, and presumably $Mo(CO)_6$ on photolysis at 195K forms $Mo(CO)_5$(alkane) which is then converted to $Mo(CO)_5(H_2O)$ by thermal reaction. On freezing to 77K, the $Mo(CO)_5(H_2O)$ associates with THF, causing the shift in the low frequency A_1 band and $Mo(CO)_6$...THF associates are also formed.

In the glyme case, after photolysis, only two bands at 1932 and 1891 cm^{-1} were observed. On cooling to 77K these bands showed the expected broadening and the lower frequency band shifted to 1870 cm^{-1}. Irradiation with unfiltered light led to complete disappearance of all carbonyl bands except trapped CO at 2136 cm^{-1}. This again is consistent with the formation of $Mo(CO)_5(H_2O)$ initially and subsequent association of this with glyme. The extremely fast photolysis at 77K is probably due initially to the replacement of two CO groups by glyme.

(iv) Triethylamine: Irradiation of $Cr(CO)_6$ and excess NEt_3 in 4:1 mch:ip at 195K using WG 335 filtered light produced a single, broad, irregularly shaped band at 1931 cm^{-1} which on prolonged photolysis developed a shoulder at 1910 cm^{-1}. Very little can be deduced from this, but as the band did not grow as the $Cr(CO)_6$ decreased possibly an insoluble product was being formed e.g. $(Cr(CO)_5(OH))(HNEt_3)$. However, attempts to repeat this reaction on a preparative scale and isolate the product resulted only in the isolation of impure $Cr(CO)_5(NEt_3)$.

(v) Small Phosphines: Triethylphosphine and triphenylphosphine are included in this category because they react quite differently from the bulkier phosphines described in section (vi). Irradiation of $Cr(CO)_6$ with WG 335 filtered light in the presence of triphenylphosphine at 195K results in the formation of an insoluble product, probably $Cr(CO)_5(PPh_3)$. However, $Mo(CO)_6$ irradiated under the same conditions produces mainly $Mo(CO)_5(PPh_3)$ which remains in solution together with some trans-$Mo(CO)_4(PPh_3)_2$ which precipitates. Irradiation of $Cr(CO)_6$ in the presence of excess PEt_3 under similar conditions resulted in the formation of a mixture of $Cr(CO)_5(PEt_3)$ and the cis and trans disubstituted compounds.

(vi) Hindered Phosphines: Triisopropylphosphine (Tip) and tricyclohexylphosphine (Tcp) behave differently from those described in section (v), presumably because of their larger size. Experiments were conducted irradiating $Cr(CO)_6$ and $Mo(CO)_6$ in hydrocarbon and CH_2Cl_2 in the presence of Tip and Tcp at 77K, 195K, and room temperature. In cases where a large excess of phosphine was used the main products, except in the 77K reactions, were $M(CO)_{6-n}(PR_3)_n$ (n=1,2) compounds, but in cases where concentrations of phosphine were of the same order of magnitude as the starting concentrations of hexacarbonyl a species with three bands similar to (I) was formed. Typical frequencies were

$Cr(CO)_6$/Tip: 2070(vw), 1932(s), and 1892(m):at room temperature in 4:1 mch:ip; $Cr(CO)_6$/Tcp: 2075(vw), 1929(s), and 1891(m) at room temperature in n-heptane. Although these bands are fairly close to bands of $M(CO)_5(PR_3)$ and $M(CO)_4(PR_3)_2$ (e.g. $Mo(CO)_5$(Tip) in 4:1 mch:ip — A_1 2065(m), A_1+E 1930(vs); trans-$Mo(CO)_4(Tip)_2$ — E_u 1879 cm^{-1}), they can be distinguished from these bands and in some spectra both the phosphine substituted species and the new bands can be observed. There are two likely possibilities for the identity of the new species (II): (i) a modified form of $M(CO)_5(H_2O)$ and (ii) a phosphine oxide complex with the phosphine oxide bonded to the metal through oxygen. Both phosphines are air sensitive, but Tip is expected to oxidise faster since it is a liquid. Species (II) formed even when Tip redistilled in vacuo and hydrocarbon solvent which had been rigorously degassed by four freeze-pump-thaw cycles were used and the solution was prepared and transferred to a sealed cell in a glove box with a dry N_2 atmosphere, and so the possibility of a phosphine oxide complex is unlikely. The main difference between (II) and (I) is the relative stability of (II) at room temperature, although attempts to concentrate solutions which presumably contained (II) resulted in the production of $M(CO)_6$ and its mono and disubstituted phosphine derivatives when CO was pumped off from the solution. Attempts to observe the ^1H n.m.r. spectrum of (II) were also unsuccessful, probably because it could only be generated in very low concentration (~10^{-2}M).

It is not surprising that the presence of a basic phosphine should stabilise $M(CO)_5(H_2O)$ since association of the phosphine with H_2O will make thermal displacement of the H_2O, or in this case the $H_2O...PR_3$ unit, which is the most likely first step in an S_n^1 type mechanism for regeneration of $M(CO)_6$, more difficult and it will hinder possible hydrogen bonding of the coordinated water to free CO which could well be the first step in an S_n^2 type substitution process.

The reaction of $Cr(CO)_6$ in the presence of Tip was the most thoroughly studied of the above reactions and will be discussed in detail. Species (II) could be produced in this case either during warm up of glass containing $Cr(CO)_5$ and Tip or by irradiation of solutions containing $Cr(CO)_6$ and Tip at room temperature or 195K. At 77K the spectrum of $Cr(CO)_6$ showed some interaction with Tip --- activation of the E_g mode and broadening of the ^{13}CO band together with the incipient splitting of the T_{1u} band which shifted to 1980 from 1983 cm^{-1} at room temperature. However, these effects were not as pronounced as in the MTHF case. Irradiation at 77K with a WG 305 filter produced $Cr(CO)_5$ with an i.r. spectrum identical to that observed in the absence of phosphine, although visible spectra were not examined. Fast warm up to 195K produced the bands of (II) together with a weak band at 1910 cm^{-1} and a shoulder on the high frequency side of the 1932 cm^{-1} band which could be due to free $Cr(CO)_5(H_2O)$. On warm up to room temperature these bands disappeared leaving only (II). Refreezing to 77K resulted in the bands of (II) collapsing to a broad hump in the 1950-1910 cm^{-1} region.

Even at 195K the $Cr(CO)_6$ spectrum shows interaction with phosphine --- activation of the E_g mode and the appearance of a shoulder on the low frequency side of the T_{1u} band and slight broadening of the ^{13}CO band. This probably indicates that the same type of interaction as occurs at 77K is occurring, but that not all the $Cr(CO)_6$ molecules are involved. This was observed with concentrations of $Cr(CO)_6$ 10^{-2}M and Tip $5x10^{-2}$M. Irradiation with WG 335 filtered light produced (II) which persisted until room temperature and then was gradually reconverted to $Cr(CO)_6$ thermally over a period of 2h. Irradiation at room temperature in n-heptane produced mainly $Cr(CO)_5(Tip)$ and trans-$Cr(CO)_4(Tip)_2$. The E_u band of the trans disubstituted compound produced in this way is split into two components at 1880 and 1870 cm^{-1}. However, irradiation of $Mo(CO)_6$ and Tcp at room temperature usually produced a species (II). The bands of the spectrum of $Cr(CO)_5(Tip)$ in methylene chloride were very broad and it was impossible to tell whether (II) was produced in that solvent or not.

(vii) <u>Phosphites</u>: $Cr(CO)_6$ was irradiated at room temperature and at 195K in the presence of $P(OPr^i)_3$. However, both $Cr(CO)_6$ and $Mo(CO)_6$ in the presence of $P(OMe)_3$ came out of solution at 195K and only irradiation at room temperature was possible. The result of this irradiation of $Mo(CO)_6$ and $P(OMe)_3$ in 4:1

mch:ip with unfiltered light was the production of mainly $Mo(CO)_5(P(OMe)_3)$ together with a small amount of trans-$Mo(CO)_4(P(OMe)_3)_2$. Irradiation of $Cr(CO)_6$ with $P(OPr^i)_3$ at both room temperature and 195K produced a similar mixture of mono and disubstituted hexacarbonyl with very little if any $Cr(CO)_5(H_2O)$.

The experiments described in sections (i)-(vii) above were carried out incidentally to the main work involved in this study and by no means constitute a systematic examination of hexacarbonyl photolysis reactions in the presence of Lewis base ligands. However, a few points of general interest are apparent from the above results. Consistent with Kelly's findings[125] acetone reacts faster than water which in turn reacts faster than THF with $Mo(CO)_5$ in hydrocarbon at 195K, yet photolysis of $Mo(CO)_6$ in the presence of MTHF at 77K led to predominantly $Mo(CO)_{6-n}(MTHF)_n$; so to produce a hexacarbonyl derivative by a low temperature photochemical reaction it would probably be better to irradiate in a glass at 77K for a simple σ donor, but better to irradiate in solution at 195K for a ligand with a π system (e.g. a ketone). However, other factors may also operate as in the case of Tip and Tcp, and the use of glass media on a preparative scale is difficult requiring long irradiation times and very fast warm up to obtain metastable products. It should also be noted that CO was not allowed to escape in any of the above reactions, but CO reacted more slowly with $M(CO)_5(alkane)$ than all the other ligands described.

(B) Non-basic Ligands

Apart from alkane which is always present, these include H_2, CS_2, CO_2, S_8, cyclooctene, and norbornadiene (NBD). The first three members of the above list are not common ligands in carbonyl complexes and are all relatively weakly bonded. S_8 forms a more stable complex and probably functions as a normal σ donor ligand although it is not normally considered basic.

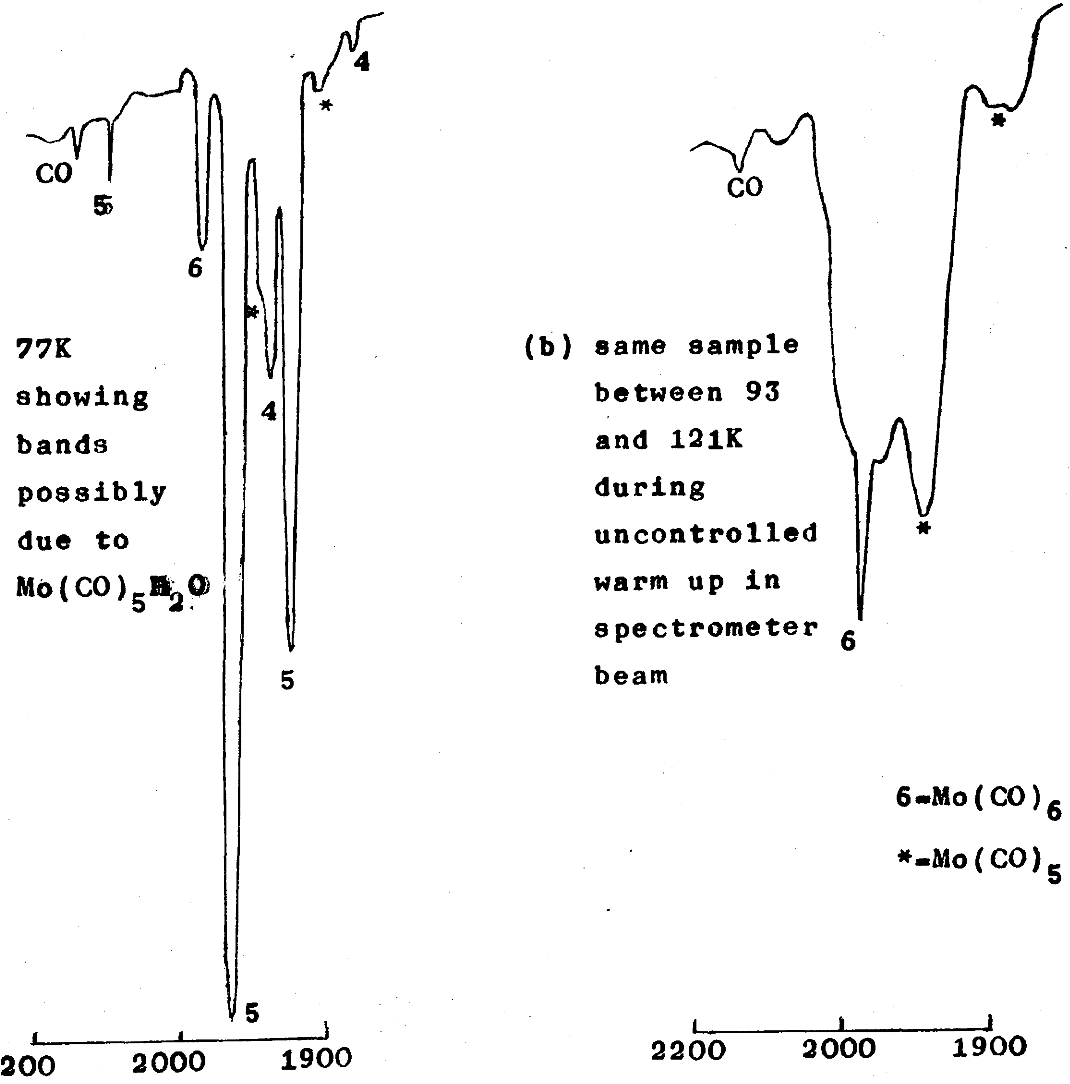
(i) Hydrogen: Photolysis in glasses made from 4:1 mch:ip solutions purged with H_2 was originally carried out to try to determine whether (I) was due to a complex of one of the atmospheric gases. However, the effect of H_2 on the reaction soon became apparent. The solubility of H_2 at p_{H_2}=1atm. in n-hexane or n-heptane at 25°C is around 4.5×10^{-3}M [50], i.e. around half the normal starting concentration of hexacarbonyl, and presumably its solubility in 4:1 mch:ip is similar. Since solutions were degassed by freeze-pump-thaw cycles and then exposed to about 1atm. of H_2 at room temperature, the concentration of H_2 in the glass is probably close to the above value.

Freezing of H_2 saturated solutions of $Cr(CO)_6$ or $Mo(CO)_6$ showed the usual signs of pre-photolytic interaction: activation of the E_g mode, which is split in this case, broadening of the T_{1u} band, and slight broadening of the ^{13}CO band. Photolysis at 77K with WG 305 filtered light was slightly faster than photolysis in the absence of H_2, but the products were similar. For example in the $Mo(CO)_6$ case the primary product showed bands at 2095(w), 1961(vs), and 1923(s) similar to $Mo(CO)_5$ in the absence of H_2. Some $Mo(CO)_4$ was also observed. A weak band at 2000 cm^{-1} was observed and is possibly due to a polymeric species similar to that responsible for the 1997 cm^{-1} band in pure 4:1 mch:ip. However, the intensity of this band did seem to depend on the concentration of primary product, unlike the polymer bands mentioned earlier, but it is important to note that the 2000 cm^{-1} band was always very weak and was close to a spectrometer grating change, and so the apparent relation of its intensity to $Mo(CO)_5$ may be fortuitous. It is not due to an M-H stretch since it was also observed in D_2 saturated glass (at 1998 cm^{-1}). The B_2 mode of $Mo(CO)_5$ is predicted at 2010 cm^{-1} from Cotton-Kraihanzel force constants, but the corresponding A' mode of eq. $Mo(CO)_4(^{13}CO)$ is observed at 1994.9 cm^{-1}, and so it is possible that this is responsible for the 2000 cm^{-1} band.

Irradiation with WG 335 filtered light of a sample with both primary and secondary products present showed photoreversal with $Mo(CO)_4$ disappearing and $Mo(CO)_6$ being regenerated, but very little change in the $Mo(CO)_5$ spectrum over 15 min. in contrast to the situation in the absence of H_2 where both unsaturated species,in similar relative concentrations, reversed to give $Mo(CO)_6$. Irradiation of $Mo(CO)_6$ in an H_2 saturated glass with WG 335 filtered light led to slow production of the same primary product as WG 305 irradiation. In some cases, where possibly wet H_2 had been used, a shoulder at 1945 cm^{-1} on the high frequency side of the 1937 cm^{-1} band of $Mo(CO)_4$ and a weak band at 1902 cm^{-1} were observed during photolysis with WG 305 and photoreversal with GG 420 filtered light. Attempts to reproduce these bands using dry H_2 were unsuccessful and so possibly these are the two lowest frequency bands of $Mo(CO)_5(H_2O)$. On glass softening the normal spectrum of $Mo(CO)_5(H_2O)$ (see fig. 3-10) together with a very broad band under the $Mo(CO)_6$ T_{1u} band, probably due to solid hexacarbonyl, is produced very quickly around 95K when some CO is still trapped in the glass. As warm up continues the spectrum gradually changes until at 195K it is similar to the $Mo(CO)_5(H_2O)$ spectrum normally observed at that temperature with some signs of splitting of the E band (1946, 1941 cm^{-1}). Even when dry H_2 was used, $Mo(CO)_5(H_2O)$ and solid hexacarbonyl formed very quickly on glass softening.

All these observations are consistent with $Mo(CO)_5$ being present in H_2 saturated glass as $Mo(CO)_5...H_2$ rather than $Mo(CO)_5$...alkane. This would explain the very fast formation of $Mo(CO)_5(H_2O)$ and solid hexacarbonyl on glass softening if H_2 were displaced from $Mo(CO)_5(H_2)$ much faster than alkane from $Mo(CO)_5$(alkane), and this is quite likely on steric grounds. The formation of $Mo(CO)_5(H_2O)$ in the glass could be explained if water associates with $Mo(CO)_6...H_2$ associates on freezing. Using wet solid $Mo(CO)_6$ for starting material does not result in association or production of $Mo(CO)_5(H_2O)$ in the glass. The identity of the 2000 cm^{-1} band is still a mystery, though it is

Figure 3-10: $Mo(CO)_6$ after irradiation in H_2 saturated 4:1 mch:ip at 77K.

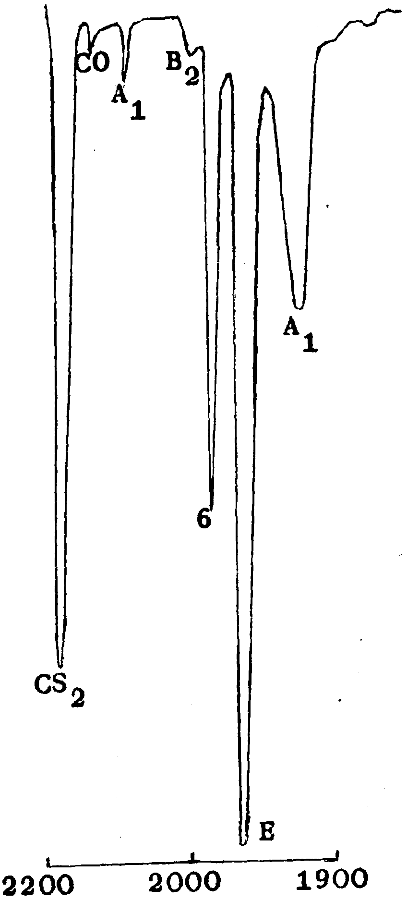


(a) 77K showing bands possibly due to $Mo(CO)_5H_2O$

(b) same sample between 93 and 121K during uncontrolled warm up in spectrometer beam

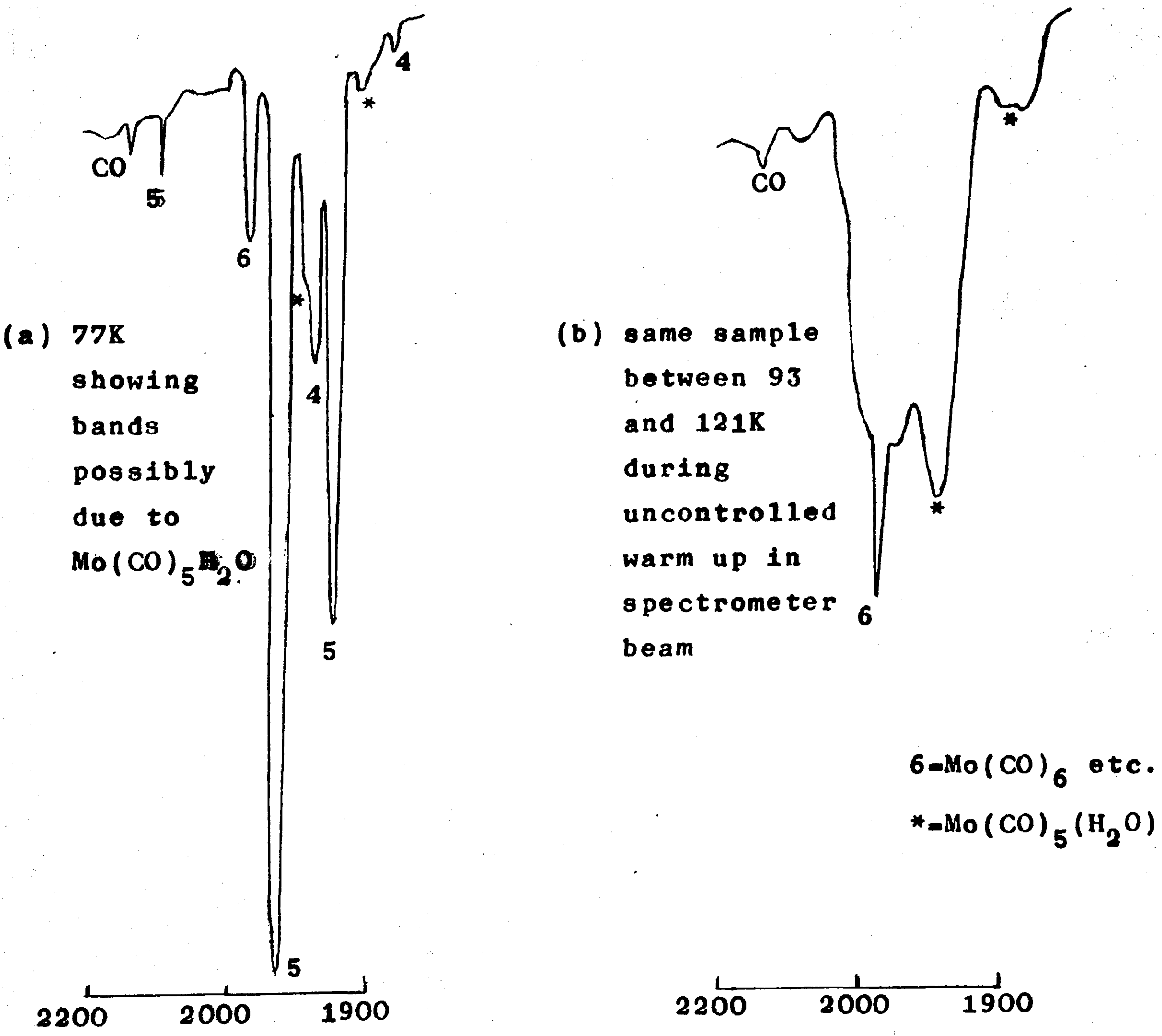
6=$Mo(CO)_6$ etc.
*=$Mo(CO)_5(H_2O)$

Figure 3-11: $Mo(CO)_5(CS_2)$ in 4:1 mch:ip at 77K.



6=$Mo(CO)_6$

Figure 3-10: $Mo(CO)_6$ after irradiation in H_2 saturated 4:1 mch:ip at 77K.



(a) 77K showing bands possibly due to $Mo(CO)_5H_2O$

(b) same sample between 93 and 121K during uncontrolled warm up in spectrometer beam

6=$Mo(CO)_6$ etc.

*=$Mo(CO)_5(H_2O)$

possibly due to $Mo(CO)_4(^{13}CO)(H_2)$.

(ii) Carbon Disulphide: Interest in photolysis of hexacarbonyls in the presence of CS_2 was aroused because of the differences between the preparation of $CpMn(CO)_2(CS)$, which can be prepared from $CpMn(CO)_2$(olefin) in CS_2 solution in the presence of PPh_3[126], and $M(CO)_5(CS)$, which is prepared from $M_2(CO)_{10}^{2-}$ and Cl_2CS.[127] In the case of $CpMn(CO)_2(CS)$ the reaction is thought to proceed through $CpMn(CO)_2$ and $CpMn(CO)_2(CS_2)$ intermediates[126], but attempts to prepare $M(CO)_5(CS)$ from $M(CO)_5L$ and CS_2 (L=olefin, THF) have been unsuccessful[134]. Photolysis of hexacarbonyls in hydrocarbon glass in the presence of CS_2 was carried out to see if any $M(CO)_5(CS_2)$ complexes were formed. CS_2 has a moderately intense absorption in the near u.v. at 318 nm and so acts to some extent as an internal filter. However, the region of the spectrum between 250 and 300 nm which includes the lowest energy charge transfer band of $M(CO)_6$ is fairly clear.

Freezing solutions of $Mo(CO)_6$ and $W(CO)_6$ in 4:1 mch:ip around 0.75M in CS_2 showed the usual signs of association of ligand and hexacarbonyl. Irradiation at 77K with unfiltered light led to the production of CO and a new species with at least four i.r. bands (Mo: 2085(w), 2000(w), 1963(vs), and 1927(m); W: 2084(w), 2073(vw), 1991(w), 1951(vs), and 1927(m)). The frequencies of the two strongest bands in each case are very close to those observed for $M(CO)_5$ in hydrocarbon glass, but the form of the spectra is slightly different (fig. 3-11). The highest frequency band is more intense relative to the strongest band than the corresponding band of $M(CO)_5$ and a small shoulder which appears on the high frequency side of this band (2090 cm^{-1} in the W case) is probably due to some $M(CO)_5$ which is not interacting with CS_2. The 2073 and 1991 cm^{-1} bands in the W case and the 2000 cm^{-1} band in the Mo case seem to be related to the other bands and are probably bands of ^{13}CO substituted species (cf. $Mo(CO)_5$ in CH_4: 1994.9; $W(CO)_5$ in CH_4: 2083.5,1986.4 cm^{-1} for bands due to equatorially substituted $M(CO)_4(^{13}CO)$[37]). The lowest frequency band is broader than the corresponding band in the absence of CS_2. The most likely formulation for the new species is $M(CO)_5(CS_2)$ with a similar structure to $M(CO)_5$(alkane). There is probably a stereospecific interaction of CS_2 with the $M(CO)_5$ vacant site since the relative intensities of the bands (especially the two A_1 bands) are different from those in $M(CO)_5$(alkane). In MTHF doped hydrocarbon, where MTHF is probably interacting with $Mo(CO)_5$(alkane) it is the $A_1^{(1)}$ band frequency rather than the band intensities which is affected by the presence of MTHF. The high frequency A_1 band of $M(CO)_5L$ can gain intensity by the $A_1^{(2)}$ mode mixing with the $A_1^{(1)}$ mode or by the four equatorial CO groups deviating from planarity[112]. These two effects are of course linked since the amount of mixing depends on electron drift during vibrations and the nature of the metal to CO bonding (especially the π bonding) will depend on the distribution of CO groups about the metal, i.e. the $C\hat{M}C$ angles.

Since in the spectra observed the bands of $M(CO)_5(CS_2)$ are probably masking bands of $M(CO)_5$(alkane), no attempt to measure relative intensities accurately or calculate bond angles was made. If θ is the angle between axial and equatorial CO groups, any deviation of θ from 90^o would be expected to produce an increase in intensity of the high frequency A_1 band; so either a large or small ligand L could be expected to cause a change in the relative intensities of the A_1 bands. However, values of θ close to 90^o have been calculated for $Cr(CO)_5(Ar)$ and $Cr(CO)_5(Ne)$, where the ligand is very small and the high frequency A_1 band is very weak indeed[90], and for $Mo(CO)_5(P(OR)_3)$ [112] where the ligand is much larger and the high frequency A_1 bands are at least as intense relative to the E band as that observed here. There are probably other effects taking place e.g. direct donation of electrons from ligand to cis CO groups[96] which affect the relative intensities of bands, but $M(CO)_5$(olefin) complexes (e.g. $W(CO)_5$(cyclooctene)) tend to have intense high frequency A_1 bands and a sideways bonded olefin is a relatively large ligand. The increased intensity of the high frequency A_1 band probably means that CS_2 is coordinated to the metal through its 'vacant' site,,but this increase in intensity does not show whether CS_2 is sideways bonded, as in $CpMn(CO)_2(CS_2)$[126], or bonded through sulphur. Phosphine sulphide complexes have bands in similar positions e.g. $Cr(CO)_5(SPPh_3)$ 2063(m), 1947(s), and 1912(m)[129] and so CS_2 could well be S bonded.

Visible spectra were not recorded, but the glass containing $W(CO)_5(CS_2)$ had a yellow colour rather than the green colour characteristic of $W(CO)_5$(alkane). No secondary photolysis products were observed after 30 min. unfiltered irradiation, by which time extensive secondary and tertiary photolysis would have been observed in the absence of CS_2. Photoreversal was not observed and irradiation of $Mo(CO)_6$+CS_2 with WG 305 filtered light, which is effectively irradiating the $Mo(CO)_6$ with light $\lambda>330$ nm since CS_2 absorbs most of the light between 305 and 330 nm, led to the production of $Mo(CO)_5(CS_2)$, though less quickly. It is possible that photolysis in the last case proceeded through absorption of light by the CS_2 part of a $Mo(CO)_6...CS_2$ associate and transfer of energy to $Mo(CO)_6$, i.e. CS_2 acting as a photosensitiser. Secondary photolysis probably proceeds through the lowest energy charge transfer transition of $M(CO)_5$ which in 4:1 mch:ip has maxima at 237 nm in $W(CO)_5$ and 245 nm in $Mo(CO)_5$, but CS_2 absorbs most of the radiation below 240 nm and so it is not surprising that secondary photolysis does not take place. Irradiation of $Mo(CO)_6$ +CS_2 with 254 nm monochromatic light (i.e. irradiating in the clear region of the CS_2 spectrum only) produced $Mo(CO)_5(CS_2)$.

On warm up the bands of $M(CO)_5(CS_2)$ gradually decrease as bands of $M(CO)_5(H_2O)$ increase, and by 175K the spectrum is the same as that observed in the absence of CS_2. No other bands were observed and there seems to be a direct ligand exchange:

$M(CO)_5(CS_2)+H_2O \longrightarrow M(CO)_5(H_2O)+CS_2$. There is a possibility that this exchange at 150K could be used to prepare $M(CO)_5L$ compounds where L is other than H_2O An experiment was tried using $Mo(CO)_6$, CS_2, and an excess of Tcp in 4:1 mch:ip, but the product observed was $Mo(CO)_5(H_2O)$...Tcp, presumably because Tcp reacts too slowly to prevent $Mo(CO)_5(H_2O)$ forming. In the thermal preparation of $CpMn(CO)_2(CS)$ [126], PPh_3 removes S from coordinated CS_2 in $CpMn(CO)_2(CS_2)$. However, the more easily oxidisable Tcp does not function in this way here and this is yet another example of how the very different conditions used in this work make relation of the results to room temperature preparative chemistry very difficult.

(iii) Carbon Dioxide: Since carbon disulphide was found to react with $M(CO)_5$, experiments were carried out to see if CO_2 would form complexes under the same conditions. However, spectra of $Mo(CO)_6$ and $Cr(CO)_6$ in CO_2 saturated 4:1 mch:ip showed very little sign of association on cooling and photolysis at 77K produced the same products as observed in the absence of CO_2. On warm up only solid hexacarbonyl and $M(CO)_5(H_2O)$ could be identified and by room temperature starting material was almost completely regenerated. It should be noted, however, that the concentration of CO_2 in the glass would certainly be very low.

(iv) Sulphur: M.J. Boylan obtained some evidence for reaction of elemental sulphur with $W(CO)_6$ in hydrocarbon[45] and so in this work $Mo(CO)_6$ and $Cr(CO)_6$ were photolysed in the presence of S_8.

Like CS_2, S_8 in hydrocarbon absorbs in the near u.v., but since a saturated solution of S_8 in hydrocarbon is only about 10^{-3}M at room temperature, the percentage of light absorbed by the sulphur is small compared to the percentage absorbed by $M(CO)_6$, and so photoreactions of S_8 or filtering by S_8 are unlikely under the conditions used.

As with other n donors association of $M(CO)_6$ and S_8 was observed on cooling. Photolysis at 77K with WG 305 filtered light gave $M(CO)_5$ and some $M(CO)_4$ identical to that produced in the absence of S_8. On warm up a very broad spectrum with 'humps' at 1970, 1950, and 1880 cm^{-1} was obtained around 103K, but by around 230K this spectrum had resolved into bands due to $M(CO)_6$ and $M(CO)_5(H_2O)$ and three new bands at 2085(m), 1966(s), and 1952(m) cm^{-1}. These bands, which are most likely due to $Mo(CO)_5(S_8)$, grew as the bands of $M(CO)_5(H_2O)$ diminished, reaching a maximum around 240K. Between 240K and room temperature the intensity of the new bands gradually decreased, but regeneration of $M(CO)_6$ was by no means complete and specks of brown solid were observed in the sample cell at room temperature. This is in contrast to $W(CO)_5(S_8)$ which persisted for some time at room temperature[45].

This type of complexation may well have a use as a mild method of activating S_8, but scaling up the reaction for preparative purposes will certainly be difficult because of the low solubility of both $M(CO)_6$ and S_8 in hydrocarbon.

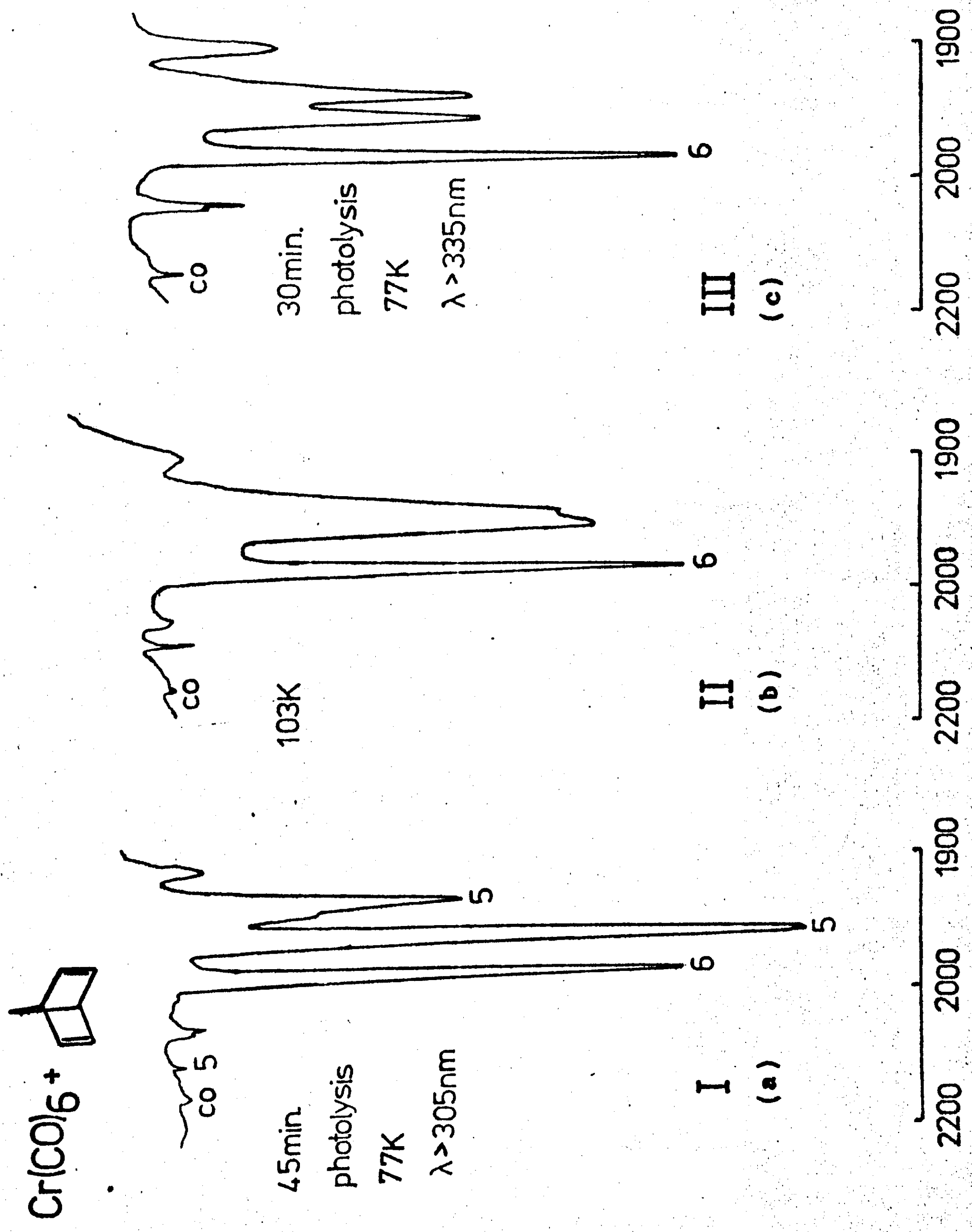
Irradiation at 195K with WG 335 filtered light results in formation of $M(CO)_5(H_2O)$. Because of the difficulty in scaling up the reaction the brown solid mentioned above was not identified and no chemical tests to establish the form of the sulphur in the complex were carried out.

Assuming the compound responsible for the new bands is in fact $M(CO)_5(S_8)$, the frequencies observed are higher than those expected from comparison with other S donor complexes, e.g. R_3PS, HR_2PS,[130] SEt_2,[131] and $(CH_2)_4S$[96]. The band positions and the sharpness of the two lowest frequency bands are similar to $M(CO)_5$(acetylene) spectra,[132] and it could well be that S_8 is bonding to the metal utilising π orbitals like an olefin or acetylene.

(v) Olefins: $Cr(CO)_6$ was photolysed at 77K in the presence of norbornadiene (NBD) and $W(CO)_6$ was photolysed under similar conditions in the presence of cyclooctene. In both cases there were signs of considerable interaction of hexacarbonyl and olefin before photolysis. In the $W(CO)_6$/cyclooctene case a large excess of cyclooctene was used and the products on irradiating at 77K were $W(CO)_5$, $W(CO)_5(C_8H_{14})$, and cis-$W(CO)_4(C_8H_{14})_2$. On warm up to 195K the main species remaining was $W(CO)_5(C_8H_{14})$ which showed three i.r. bands at 2090(m), 1957(s), and 1942(vs). These are assigned to the $A_1^{(2)}$, $A_1^{(1)}$, and E modes respectively, and the reversal of the usual ordering in the frequencies of the $A_1^{(1)}$ and E modes is typical of $M(CO)_5$(olefin) complexes[132]. Two bands at 2035 and 1890 cm^{-1} which persist at 195K are assigned to cis-$W(CO)_4(C_8H_{14})_2$, the other two bands of which are probably masked by the bands of the monosubstituted compound. The trans disubstituted compound may also be present since it will almost certainly have one i.r. band around 1950 cm^{-1} [132] which would also be masked. A band at 1910 cm^{-1} present at 195K is probably due to $W(CO)_5(H_2O)$. Warm up to room temperature resulted in some regeneration of hexacarbonyl, but $W(CO)_5(C_8H_{14})$ still persisted.

$Cr(CO)_6$ was photolysed in the presence of norbornadiene to try to identify some of the compounds formed in the photolysis of the hydrogenation catalyst $Cr(CO)_4(NBD)$ which will be discussed more extensively in the next chapter. When a solution of $Cr(CO)_6$ (10^{-2}M) and NBD (0.25M) in 4:1 mch:ip was frozen to 77K, the usual signs of association were observed. Photolysis with WG 305 filtered light led to production of $Cr(CO)_5$ mostly, but a band at 1905 and a shoulder on the $Cr(CO)_5$ A_1 band at 1940 cm^{-1} which are probably due to $Cr(CO)_4(NBD)$, and a broad feature around 2040 cm^{-1} were also observed. Warm up to 93K followed by refreezing produced a spectrum with a weak band around 2075 cm^{-1} and a broad irregularly shaped band at 1950 cm^{-1} (fig. 3-12) together with the $Cr(CO)_6$ and $Cr(CO)_4(NBD)$ bands. There was very little regeneration of $Cr(CO)_6$ at this stage. Photolysis of this refrozen glass with WG 335 filtered light led to production of $Cr(CO)_4(NBD)$. On warm up to room temperature

Figure 3-12: $Cr(CO)_6$+norbornadiene in 4:1 mch:ip at 77K.



most of the $Cr(CO)_6$ was regenerated. The broad band around 1950 cm^{-1} is probably due to $Cr(CO)_5(NBD)$ and possibly a small amount of $Cr(CO)_5(H_2O)$..Frequencies of 1955 and 1935 cm^{-1} have been quoted for the two strongest bands of $Cr(CO)_5(NBD)$ in hexane at room temperature[133]. In the spectrum produced on irradiation of $Cr(CO)_5(NBD)$ containing glass (fig. 3-12(c)) there is a shoulder at 2041 cm^{-1} on the high frequency side of the 2037 cm^{-1}, high frequency A_1, band of $Cr(CO)_4(NBD)$ which is not present in the spectrum of pure $Cr(CO)_4(NBD)$ in glass. From its position this band could be due to a small amount of unsaturated $Cr(CO)_4(NBD)$ i.e. a sixteen electron species with NBD bonding through only one olefinic moiety and a vacant site, or possibly a coordinated alkane cis to the olefin. On warm up to 98K and refreezing this shoulder disappears. The relevance of these results to the photolysis of $Cr(CO)_4(NBD)$ and its use as a hydrogenation catalyst[133] will be discussed in the next chapter.

Conclusion

As in the $Fe(CO)_5$ case, photolysis of hexacarbonyls in pure hydrocarbon glass does not give much information about the real nature of the fragments produced when considered in isolation, but a comparison of the results with those obtained in a variety of gas matrices shows that the reactions in hydrocarbon are basically the same as those in other 'inert' matrices. The term 'inert' matrix used here refers to the types of weakly interacting matrix[90] which have been previously considered inert, e.g. Ar, Xe, CH_4, hydrocarbon glass. Photolysis in the strongly interacting MTHF glass shows the expected stepwise replacement of CO by MTHF.

The photolysis reactions in the presence of potential ligands described above do not give a comprehensive view of the field by any means and there is still room for several systematic studies of hexacarbonyl photolysis in the presence of specific classes of ligands. However, several general features have emerged from the reactions described above. For example the importance of $M(CO)_5$...alkane association in reactions in the glass and of $M(CO)_5(H_2O)$ in low temperature solution reactions has not been previously recognised. Pre-photolytic association has been shown to be important in all cases, and where no such association takes place, as in the cases of CO_2 and H_2O no complex is formed ($M(CO)_5(H_2O)$ is nearly always formed, but attempts to increase the yield by adding H_2O have been unsuccessful). The rate of displacement of alkane from $M(CO)_5$(alkane) to form $M(CO)_5L$ is dependent on the nature of L (in solution at least) and a series can be constructed: $\text{olefin} \sim CS_2 > \text{acetone} > PPh_3 \sim PEt_3 > H_2O > \text{THF} > \text{Tip} \sim \text{Tcp} > S_8 > CO$. This is fairly consistent with Kelly's results[125] for room temperature solution reactions. However, reactions occurring immediately on glass softening depend on other factors such as the degree of association in the glass before photolysis and the relative rates of substitution and polymerisation of fragments, though the polymerisation of fragments associated with potential ligands seems slow compared to $M(CO)_5L$ or $M(CO)_5(H_2O)$ formation in most cases since the polymeric species observed in pure hydrocarbon were usually not observed on glass softening in the presence of added donors.

CHAPTER 4

SUBSTITUTED GROUP VI HEXACARBONYLS

Introduction

This chapter follows naturally from chapter three, the last section of which dealt with the formation or non-formation of substituted hexacarbonyls in glasses or from fragments generated in glasses. The main class of compounds investigated was the monosubstituted phosphinocarbonyls since a considerable amount of work on the u.v./visible and i.r. spectra and the preparation of these compounds had already been done in this department[21,148], and for the most part they are air stable and present no handling problems. Other systems investigated were trans-disubstituted phosphinocarbonyls and norbornadiene-chromium tetracarbonyl, the last being of interest because of its use as a hydrogenation catalyst which produces an unusual amount of 1,2 addition of H_2 in norbornadiene and conjugated dienes[133]. Attempts to examine cis disubstituted phosphinocarbonyls in hydrocarbon failed because of their insolubility.

Like $Fe(CO)_5$ monosubstituted and cis disubstituted hexacarbonyls contain two distinct sets of CO groups and so there is a possibility of two types of primary product being formed if the basic structure is retained after photolysis. There is also a possibility of dissociation of ligand rather than CO although this is unlikely in a glass for reasons discussed in Ch.1. There are no quantitative energy level diagrams available for substituted hexacarbonyls, and there is no general agreement as to the nature of the electronic transitions most likely to

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* for references 135-147 see Chapter 5.

be responsible for the photolysis. but the results described in this chapter show that some of the apparent disparities in previous theory can be rationalised.

Spectra of $M(CO)_5PR_3$ in Hydrocarbon Glass (R=alkyl, H, alkoxide)

As with all other systems investigated, solutions of $M(CO)_5(PR_3)$ compounds show considerable changes in the CO stretching i.r. spectrum on freezing to 77K. In many cases these effects are more pronounced here because of the relatively large size of the molecules. However, the type of effect observed does not seem to depend on molecular size. Trialkyl phosphines were perhaps the bulkiest ligands used and tricyclohexyl, triisopropyl, and tri-n-butyl were selected as representative examples. The Mo complexes will be discussed in detail only since Cr and W complexes had been previously shown to behave similarly[45]. The room temperature spectra of $Mo(CO)_5(PR_3)$ compounds (R=alkyl) all show two main bands: a very sharp A_1 band at around 2070 cm^{-1} and a much more intense, broader band around 1935 cm^{-1} due to a composite of the E and low frequency A_1 bands (see fig. 4-1 and table 4-1). There are also minor features: a weak shoulder on the low frequency side of the A_1 band due to ^{13}CO substituted species[149], a weak band around 1980 cm^{-1} due to the i.r. forbidden B_2 mode, the corresponding A' mode of the equatorially ^{13}CO substituted species, and in some cases a hexacarbonyl impurity, and a weak band around 1910 cm^{-1} due to modes involving mainly ^{13}CO stretching.

Figure 4-1: $Mo(CO)_5(Tcp)$ in 4:1 mch:ip.

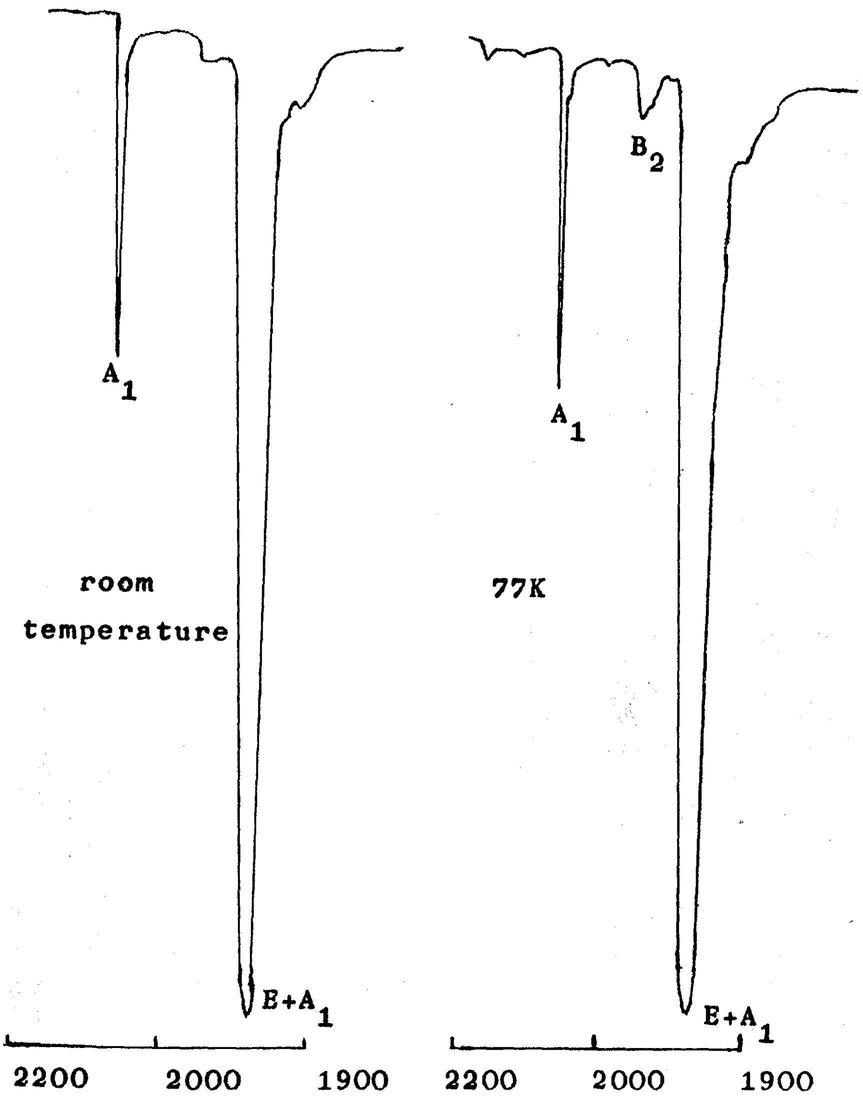


Table 4-1: Frequencies of $LMo(CO)_5$ bands in 4:1 mch:ip.

L	A_1	B_2	E	A_1	A_1	B_2	E	A_1
Tcp	2065	1976	1935		2067	1978	1932	
Tip	2067	----	1940		2067	1980	1936	
$P(n-C_4H_9)_3$	2067	----	1945		2070	1985	1940	
$P(p-C_6H_4CH_3)$	2068	1995	1949		2070	1988	1949	1940
PH_3	2081	1986	1958		2083	1990	1961	
$P(OPr^i)_3$	2076	2000	1945	1963	2080	2000	1945 1932	1955
	room temperature				77K			

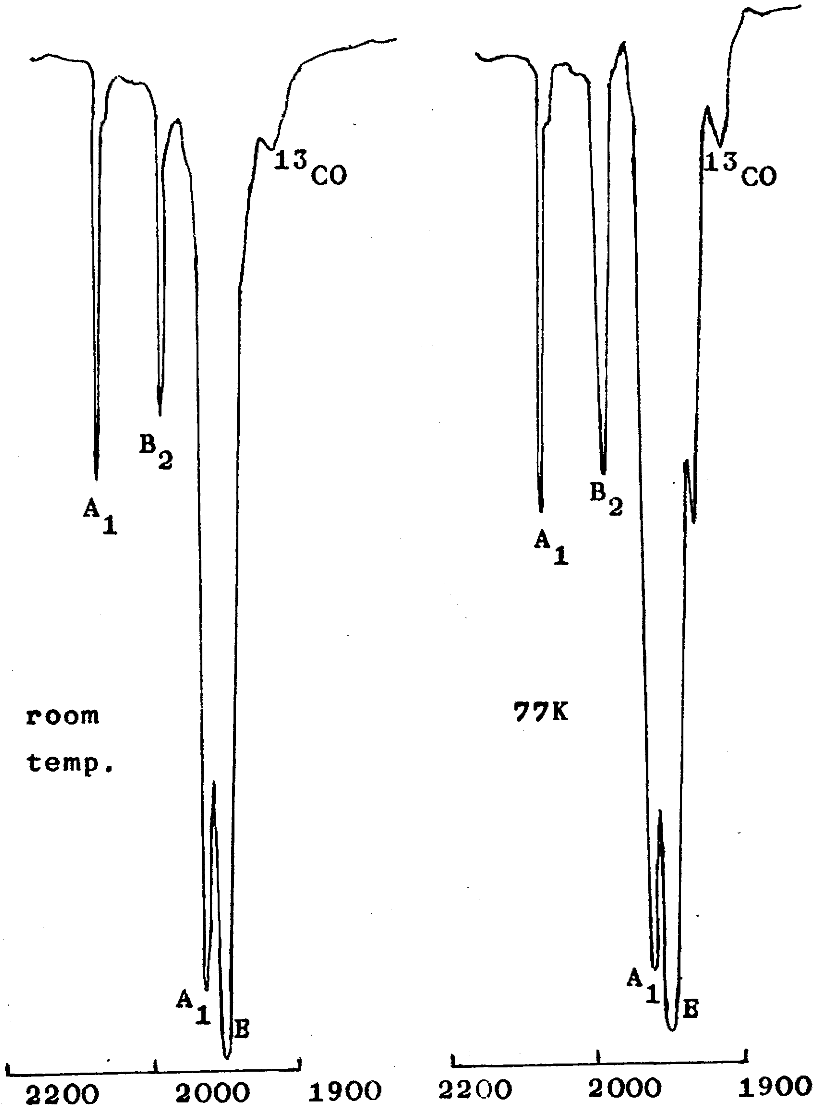
frequencies in cm^{-1}.

On cooling to 77K the high frequency A_1 band becomes sharper and the low frequency shoulder more clearly resolved, but its frequency does not change much. The band around 1980 cm^{-1} sharpens and sometimes resolves into two components, and the band around 1935 cm^{-1} becomes broader and shifts to lower frequency, while the low frequency ^{13}CO stretching band becomes less well resolved, probably because of its proximity to the E/A_1 band. In the $Mo(CO)_5(Tcp)$ case the apparent broadening is similar to that observed for the E' band of $Fe(CO)_5$ and the T_{1u} bands of hexacarbonyls, i.e. there is incipient splitting of the E band, and the band is asymmetric with a tail on the low frequency side (fig. 4-1), so that the A_1 band may resolve slightly at low temperature. In the $P(n\text{-}C_4H_9)_3$ and Tip cases, however, the broadening, which was most pronounced in the Tip case, seems to be of the type which would be expected to occur in a solution spectrum when the temperature was increased, i.e. a normal i.r. band shape is retained, but there is more intensity in the wings of the band. The reason for this is not at all clear.

$Mo(CO)_5(PH_3)$ bands show similar changes to those observed in $Mo(CO)_5(Tcp)$, the main differences being due to the much less intense high frequency A_1 and much more intense B_2 modes of $Mo(CO)_5(PH_3)$. $Mo(CO)_5(PH_3)$, however, was unique in that the starting solution showed thermal decomposition even during freezing in the dark, so that some CO was always observed in the glass even before photolysis. A P-H stretching band could be observed at 2335 cm^{-1} in the 77K spectrum of $Mo(CO)_5(PH_3)$, but this band was very much weaker than most of the CO stretches and was not observed at room temperature, even at concentrations of 10^{-1}M. It should be noted that it was possible to use concentrations of up to about 2×10^{-1}M for most of the phosphine substituted molybdenum hexacarbonyls and obtain spectra in glasses before and after photolysis similar to those observed in more dilute glasses, but the data quoted in this chapter is nearly all for concentrations of around 10^{-2}M; so direct comparison with other systems is possible. $Mo(CO)_5(P(p\text{-}C_6H_4CH_3)_3)$ is less soluble, but behaves similarly to $Mo(CO)_5(Tcp)$ on cooling, except that the low frequency A_1 band shows as a distinct shoulder in the 77K spectrum in that case. Incidentally $Mo(CO)_5(PPh_3)$ is too insoluble to isolate in hydrocarbon glass.

$Mo(CO)_5(P(OPr^i)_3)$ and $W(CO)_5(P(OPr^i)_3)$ were the only two phosphite substituted complexes investigated in this work, although very similar spectra were obtained by M.J. Boylan for $Cr(CO)_5(P(OPr^i)_3)$ and $P(OEt)_3$ substituted compounds[45]. $P(OMe)_3$ substituted compounds were also investigated by him, but their spectra at 77K are very broad and not readily interpreted. $Mo(CO)_5(P(OPr^i)_3)$ and its W analog show five bands in the room temperature spectra: a high frequency A_1 band around 2080 cm^{-1}, a B_2 band around 2000 cm^{-1}, a low frequency A_1 band around 1950 cm^{-1} overlapping with a more intense E band around 1938 cm^{-1}, and a ^{13}CO band around 1915 cm^{-1} (see table 4-1 and fig. 4-2). On cooling all the bands sharpen slightly, except the E band which broadens in the W case and splits into two components,

Figure 4-2: $Mo(CO)_5(P(OPr^i)_3)$ in 4:1 mch:ip.



one considerably sharper and less intense than the other, in the Mo case. A shoulder due to ^{13}CO substituted species is also observed on the low frequency side of the high frequency A_1 band. The uneven splitting of the E mode is unusual for a metal carbonyl derivative isolated in a glass; the effects observed in $Fe(CO)_5$ and $CpMn(CO)_3$ suggest that the E modes are tending to split into two equally intense components. The lower frequency, less intense component is very sharp (no half width can be measured as it overlaps the band due to the other component) while the more intense component appears broader near its peak than the combined band before cooling. At first it was thought that the low frequency band was mainly due to the $A_1^{(1)}$ mode and the room temperature spectrum had been misassigned previously[21]. Approximate force constant calculations were carried out assuming orderings of frequencies (i) $A_1 > B_2 > A_1 > E$ and (ii) $A_1 > B_2 > E > A_1$ and making the single assumption $k_t = k_c + k_c'$.[157] The results are shown in table 4-2.

<u>Table 4-2</u>:

(i) A_1 2080 B_2 2000 E 1945, 1932 A_1 1955 (cm^{-1})

$K_1 = 15.11$ $K_2 = 16.13$ $k_t = 0.85$ $k_c = 0.41$ $k_c' = 0.44$ (md/A)

(ii) A_1 2080 B_2 2000 E 1955,1945 A_1 1932 (cm^{-1})

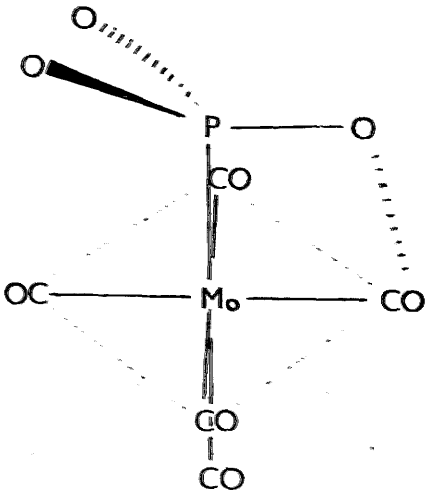
$K_1 = 14.83$ $K_2 = 16.14$ $k_t = 0.79$ $k_c = 0.39$ $k_c' = 0.40$ (md/A)

Both methods give reasonable values for parameters, but in case (ii) K_1, the stretching force constant for the CO group trans to the phosphite is exceptionally low for a compound with a π accepting substituent[131].

Correlation diagrams for $M(CO)_{6-n}(P(OMe)_3)_n$ systems[123] also predict the ordering of frequencies as in (i), and so (i) is probably the correct ordering of frequencies for $Mo(CO)_5(P(OPr^i)_3)$. For E bands the mean frequencies (i) 1938.5 and (ii) 1950 cm^{-1} were used in the calculations.

Bigorne et al. have described the splitting of E modes in various $M(CO)_{n-1}(P(OR)_3)$ compounds, including $Mo(CO)_5(P(OMe)_3)$, and suggested that there is a specific interaction between one P-O bond and an equatorial CO group[150]. However, the splitting they observed in $Mo(CO)_5(P(OMe)_3)$ in hydrocarbon solution at room temperature was around 3 cm^{-1} as opposed to the 12 cm^{-1} observed here, and the band was split into two components of equal intensity. The effect observed here can be explained if a much stronger interaction between one CO and a P-O bond than that proposed by Bigorne is taking place so that the symmetry of the molecule is lowered from C_{4v} to C_s. A structure such as that shown in fig. 4-3 would give rise to two stretching modes of the equatorial CO groups which would give bands of approximately the same frequency as the E band observed in solution spectra, but with two different intensities. The structure shown is of course not the only possibility and investigations of the δM-C-O and P-O stretching regions of the i.r. spectrum would help to clarify this. The failure to observe a similar effect in $W(CO)_5(P(OPr^i)_3)$ in glass is consistent with the above explanation since a larger central metal would increase the CO phosphite separation.

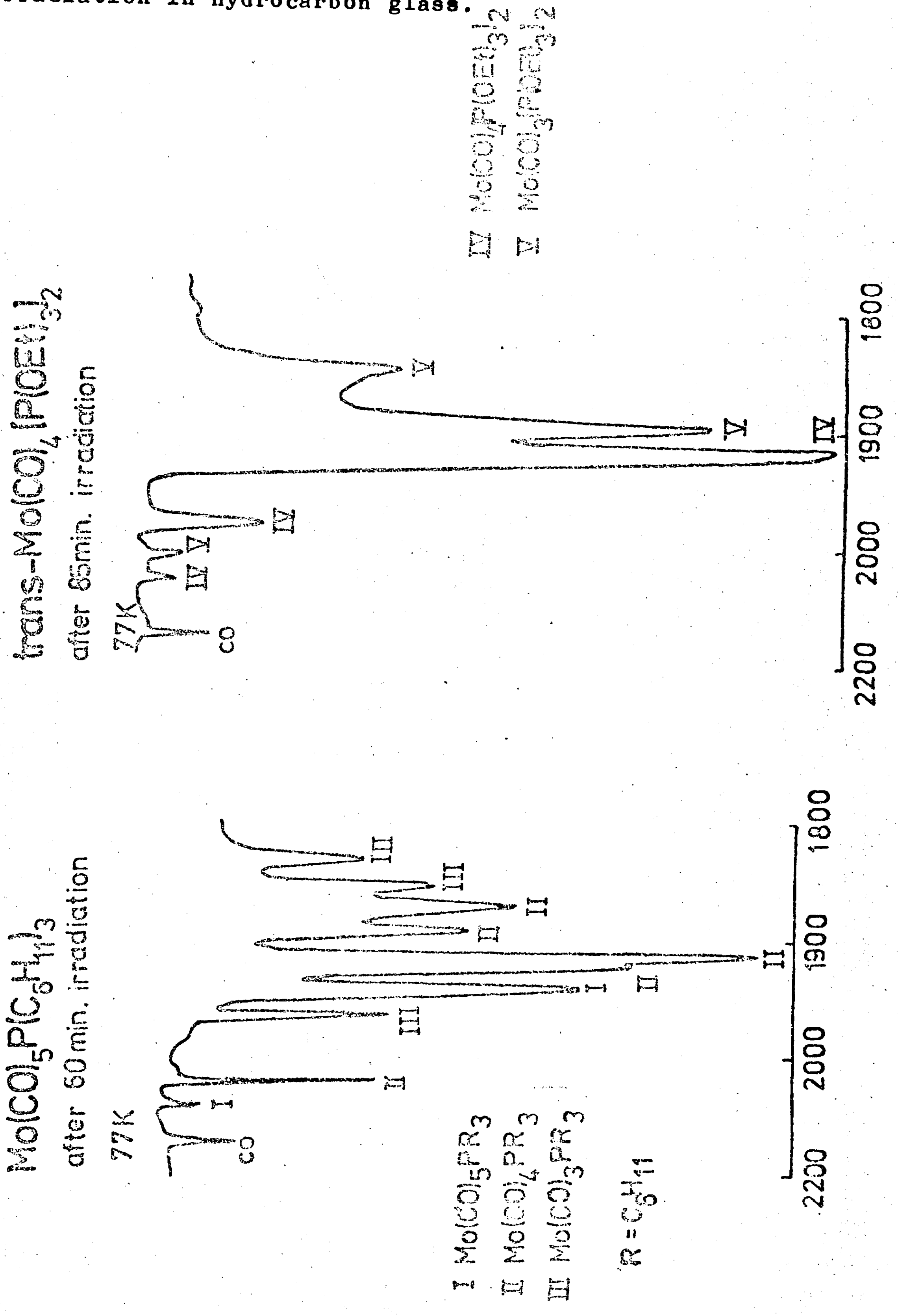
Figure 4-3:



Photolysis of $Mo(CO)_5(PR_3)$ in Hydrocarbon Glass

In all cases where R=alkyl, H, aryl, or OPr^i photolysis in hydrocarbon glass was found to yield a mixture of products, the composition of which depended on the wavelength of the irradiating light, and CO. The u.v./visible spectra of most of the compounds had previously been investigated in hydrocarbon glass at 77K and a number of bands in the near u.v. had been assigned to either d--d or metal to CO charge transfer transitions[21]. Both these types of transition can lead to photolysis, but the charge transfer is likely to be the more important at low temperature at least. However, since there is always considerable overlap of bands, it is probably impossible to specifically excite one transition and study the photolysis due to that transition. Also the processes observed in the glass will depend on the physical properties of the glass. However, it was possible to vary the composition of the product mixtures by varying the wavelength of the irradiating light. No plots of relative quantum efficiency of production of a particular species against

Figure 4-4: $Mo(CO)_5(Tcp)$ and trans-$Mo(CO)_4(P(OEt)_3)_2$ after irradiation in hydrocarbon glass.



wavelength could be made since lamp performance was by no means reproducible and very few of the i.r. bands observed did not overlap with bands of either starting material or other products. Products were identified by their relative rates of production and photoreversal, and in some cases could be interconverted with low energy light. No u.v./visible spectra of products were obtained.

The most easily interpreted spectra were obtained for $Mo(CO)_5(Tcp)$ and this system will be discussed in detail first. Irradiation at 77K in 4:1 mch:ip glass with light of wavelength 360 nm produced initially five new i.r. bands (see table 4-3 for frequencies) four of which appear to be due to one species, although the relative intensities were impossible to measure because of band overlaps. CO was observed in the glass, but there was no sign of $Mo(CO)_5$ bands. The unique band at 1883 cm^{-1} was due to a much more photosensitive species than the other four and gradually disappeared in the visible light of the spectrometer beam. It could also be destroyed by irradiation with low energy (GG 420 filtered) light or high energy (unfiltered or 254 nm monochromatic) light. The species with four bands,(I), is most likely cis-$Mo(CO)_4(Tcp)$(alkane) since the band pattern is similar to that normally observed for a cis disubstituted hexacarbonyl[76,98]. The second species, (II), is assigned as trans-$Mo(CO)_4(Tcp)$(alkane), although the second band expected for this species, which is expected to be very weak, was never observed. A C_{3v} $Mo(CO)_4(Tcp)$ species would have three i.r. bands

Table 4-3: Frequencies of LM(CO)$_4$(alkane) bands.

L	cis				trans
Tcp	2027.5	1916	1907	1864	1883
Tip	2030	1920	1912	1867	1887
P(n-C_4H_9)$_3$	2030	1926	1914	1870	1891
P(p-$C_6H_4CH_3$)$_3$	2039	1928	1921	1870	1905
PH_3	2044	1938	1930	1890	1915
P(OPr^i)$_3$	2041	1944	1924	1876	1910

in an approximate ratio of 1:1:8 [56] and so it is unlikely that the one band observed is due to such a species.

Both species were observed under all irradiation conditions used. However, the largest concentration of (II) relative to (I) was obtained on irradiation with 301 nm monochromatic light. In that case the ratio of (II):(I) remained fairly constant throughout the irradiation, but on irradiation with WG 305 filtered light larger amounts of (I) were produced in the early stages of irradiation and so there must be photoinitiated conversion of (I) to (II). It is difficult to tell whether low energy GG 420 light promotes the reverse process since the disappearance of (II) under these conditions is always accompanied by photoreversal and so it may be that (II) photoreverses faster than (I).

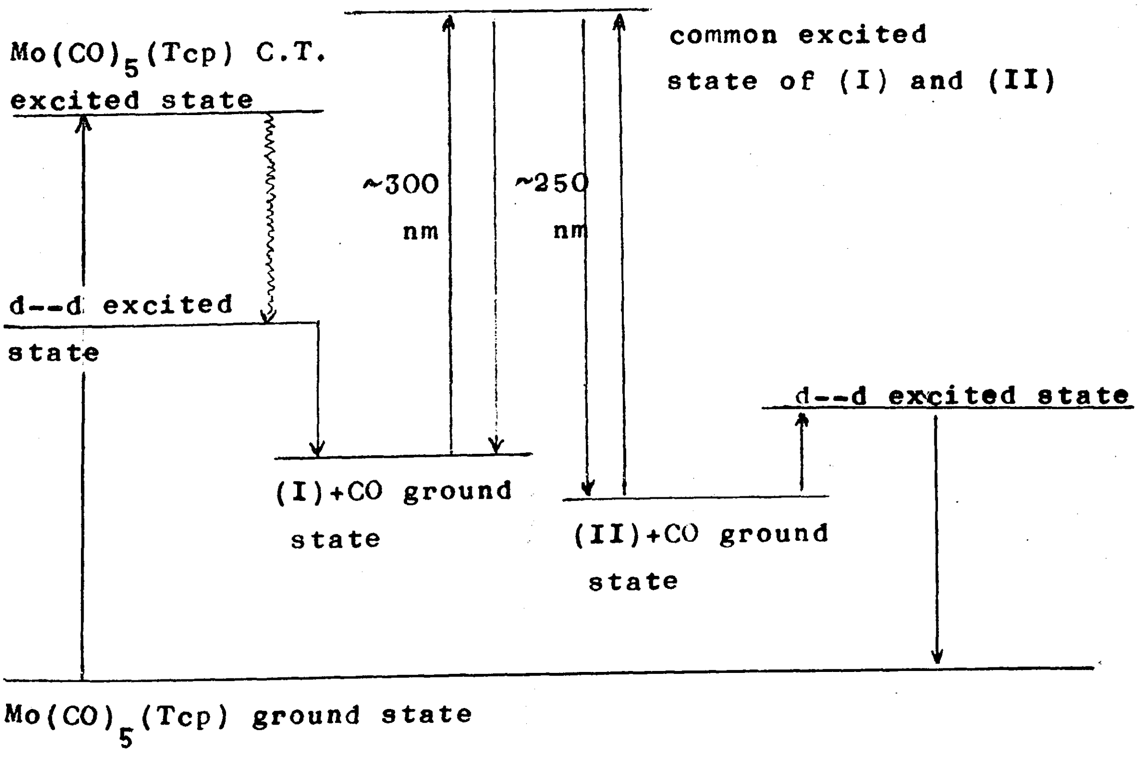
On glass softening (I) disappears at around 103K with some regeneration of starting material while (II) persists, possibly in increased concentration, until at least 113K. Since another species formed in warm up (probably $Mo(CO)_4(Tcp)(H_2O)$), has its strongest band at the same frequency as (II), it is difficult to tell if there is actually interconversion of (I) to(II) at this stage.

Irradiation in the glass for long periods with unfiltered or 254 nm monochromatic light produced a secondary photolysis product with three bands at 1955, 1847, and 1824 cm^{-1} (see fig. 4-4) which is most likely to be fac-$Mo(CO)_3(Tcp)(alkane)_2$, (III), from the band positions and relative intensities. However, prolonged irradiation (>4h) with 301 nm monochromatic light does not produce much of this species and subsequent irradiation with 254 nm monochromatic light causes a reduction in the intensity of the starting material and (II) bands and an increase in the (I) concentration only in the early stages. Later, as the (I) concentration builds up, (III) is produced. It seems, therefore, that (III) is produced from (I) only and that when (II) disappears on irradiation with 254 nm monochromatic light it is converted to (I). This seems reasonable since loss of CO from trans-$Mo(CO)_4$(Tcp)(alkane) would yeild the mer tricarbonyl.

There therefore seems to be a genuine photochemical isomerisation between (I) and (II), the formation of (I) being favoured by high energy light. A scheme has been proposed for $W(CO)_5$(pyridine) by Wrighton[118] in which, for photolysis via d--d transitions at least, low energy light will cause labilisation of the C_{4v} axis i.e. preferential loss of CO trans to the ligand in the glass, while higher energy light will cause labilisation of equatorial CO groups. This view is supported by the increased quantum efficiency for substitution of a second pyridine in $M(CO)_5$(pyridine) when 366 rather than 436 nm irradiation is used[151], since when the C_{4v} axis is labilised in solution there is more chance of losing ligand than CO. This view is also consistent with the results for $Co^{(III)}$ compounds[48,49] mentioned in chapter 1. However, in this case there is bound to be photolysis via charge transfer transitions and it has been suggested that the lowest energy charge transfer should be from the metal to the four equatorial CO groups^{21}, and radiationless decay of such charge transfer excited states could lead to the preferential formation of high energy d--d excited states and hence (I).

Thus it seems that a possible mechanism here is that the main species produced by charge transfer photolysis is (I) and that (II) is mainly produced from (I) via an absorption around 300 nm, although some (II) may be produced directly from starting material, possibly via a d--d transition. The (II) can then be reconverted to (I) via a high energy transition around 250 nm (i.e. the reverse of its production) or photoreverse to starting material via a low energy d--d transition. This mechanism would also explain the persistence of (II) after glass softening as its ground state will be more thermodynamically stable than (I) (see fig. 4-5).

Figure 4-5:



Results of photolysis in the other $LM(CO)_5$ systems studied and in those studied by M.J. Boylan were qualitatively similar. Primary photolysis produced two species: cis and trans $LM(CO)_4$(alkane), the trans being the more photosensitive. In the case of the other trialkyl phosphines (Tip and $P(n\text{-}C_4H_9)_3$) and tri-p-tolylphosphine the effects observed were almost exactly similar. In these cases, however, the strongest band of cis-$LM(CO)_4$(alkane) showed a slight increase in intensity when a product mixture was irradiated with GG 420 filtered light, but the highest and lowest frequency bands either did not change or decreased. This probably occurred because the E band of starting material was increasing due to photoreversal and the two medium frequency bands of cis-$LM(CO)_4$(alkane) overlap with the wings of this band. However, the formation of yet another species during low energy irradiation cannot be ruled out.

In the case where $L=PH_3$ the situation is more complicated since thermal decomposition of the starting material occurs even during freezing of the starting solution; so there is always CO and possibly free PH_3 present in the glass. In addition the product bands overlap extensively and so spectra are very difficult to analyse. However, some interesting features were apparent. Photolysis with WG 305 filtered light always produced a band around 2090 cm^{-1} which is at higher frequency than the high frequency A_1 band of $Mo(CO)_5(PH_3)$ at 2085 cm^{-1} and so is unlikely to be due to any $Mo(CO)_4(PH_3)L$ compound. It is, however, around the right frequency for the high frequency A_1 band of $Mo(CO)_5$ in hydrocarbon and the other bands of $Mo(CO)_5$ would be masked by the $Mo(CO)_5(PH_3)$ E and low frequency A_1 band at 1958 cm^{-1} and bands due to other photolysis products in the 1920 cm^{-1} region. It seems, therefore, that PH_3 may be lost from $Mo(CO)_5(PH_3)$ in the glass. There is also a possibility that P-H bonds are broken in the photolysis since PH_3 absorbs in the near u.v.[152]. Among the other photolysis products, which give at least three bands in the 1950-1910 cm^{-1} region and a band at 1892 cm^{-1}, there is one band at 1915 cm^{-1} which persists on warm up to 103K and disappears fastest on irradiation with low energy light and is probably due to trans-$Mo(CO)_4(PH_3)$(alkane). The cis compound is probably also present. In this case warm up to room temperature results in the production of a mixture of starting material, $Mo(CO)_6$, and cis-$Mo(CO)_4(PH_3)_2$, whereas in the other cases examined warm up resulted in regeneration of nearly all the starting material.

In the triisopropylphosphite cases again the results are qualitatively similar to those for $Mo(CO)_5$(Tcp) with both cis and trans primary products being formed. Here too the trans product disappears faster on irradiation with low energy light, but there is no significant change in the cis:trans ratio on irradiation with high energy light. This not entirely unexpected since the cis and trans compounds will be very similar electronically since $P(OPr^i)_3$ is much more like CO in its σ

donor and π acceptor properties than a trialkyl phosphine. However, it is rather surprising that the trans should still photoreverse much faster than the cis form since the selective labilisation of one axis by the lowest energy d--d transition is thought to depend on there being a significant difference in ligand field strength between ligands on that axis and ligands in the rest of the molecule[48,118]. The reason for the faster disappearance of trans in this case is not clear unless there is photoisomerisation between the two forms which is promoted by low energy light. Such a process may also occur for (I) and (II) in the Tcp case, but the evidence available does not show that it definitely does. Orientated $Cr(CO)_5$ has been generated in a matrix by polarised photolysis and the orientation can be changed by low energy light[104]. This presumably occurs by a process analogous to the photoisomerisation described here.

Warm up experiments were carried out on $M(CO)_5(P(OPr^i)_3)$ M=Mo,W, and $Mo(CO)_5(Tcp)$. All three cases showed the same sequence of events: the cis-$M(CO)_4(PR_3)$(alkane) compound disappeared together with some CO between 100 and 115K while some starting material was regenerated, then the trans photolysis product disappeared around 113K, and the three bands due to a new species which had begun to form around 100K became the main features of the spectrum apart from the starting material bands. These new bands at 2038, 1910, and 1855 cm^{-1} in the

$Mo(CO)_5(P(OPr^i)_3)$ case, 2025, 1902, and 1845 cm^{-1} in the $W(CO)_5(P(OPr^i)_3)$ case, and 2010, 1890, and 1835 cm^{-1} in the $Mo(CO)_5(Tcp)$ case are all fairly broad. On warm up to 195K they all sharpen and in the $Mo(CO)_5(P(OPr^i)_3)$ case a shoulder appears on the high frequency side of the 1910 cm^{-1} band at 1925 cm^{-1}, and a band is observed at 1865 cm^{-1}. Similar spectra can be obtained by irradiating with WG 335 filtered light at 195K in 4:1 mch:ip or n-heptane, except that in the $W(CO)_5(P(OPr^i)_3)$ case the lowest frequency band is sharper and appears at 1860 cm^{-1} then. Similarly in the $Mo(CO)_5(Tcp)$ case the lowest frequency band was observed at 1855 cm^{-1} when the solution in 4:1 mch:ip was irradiated at 195K and the band at 1890 cm^{-1} was split into two approximately equal components at 1900 and 1890 cm^{-1}, but on freezing to 77K the lowest frequency band shifted to 1835 cm^{-1}. This shift was reversible. Since this behaviour is very similar to the behaviour of $M(CO)_5(H_2O)$, it seems likely that the species involved here is cis-$LM(CO)_4(H_2O)$. Warm up to room temperature resulted in the regeneration of starting material.

Room temperature photochemical reactions of $M(CO)_5(PR_3)$ compounds in hydrocarbon solution in pyrex apparatus have been studied by Darensbourg[148], but the results seem to indicate that the final products do not depend on the primary photolysis processes. For example in photoreactions of $M(CO)_5(PR_3)$ R=Ph, with amines the final products are always cis disubstituted $M(CO)_4(PR_3)(NR_3)$, but the products of reactions with PPh_3 and

^{13}CO are trans. It is probably the case in the amine reactions that when an amine substitutes in a site trans to PR_3 the product then photolyses to lose either amine or phosphine, so that the concentration of the more photostable cis compound builds up as the reaction goes on. The ready formation of $LM(CO)_4(H_2O)$ in low temperature solution means that it will be difficult to use cooling as a method of controlling photoreactions of $M(CO)_5(PR_3)$ compounds.

Unfortunately all the $M(CO)_5L$ compounds where L=hard base available were unsuitable for photolysis in hydrocarbon glass. $Mo(CO)_5(NH_3)$ and $Mo(CO)_5$(pyridine) were too insoluble, while $Mo(CO)_5(NR_3)$ compounds were difficult to free from traces of free amine since they decomposed on silica and alumina columns or during vacuum sublimation. The room temperature photoreactions such compounds have been studied more extensively[118,153] and there seems to be a definite preference for loss of ligand rather than CO with relatively low energy light ($\lambda > 366$ nm). Probably the closest system in this work to such systems is $Mo(CO)_6$/MTHF in hydrocarbon where there may well be photolysis of $Mo(CO)_5$(MTHF) to give $Mo(CO)_5$ and MTHF in the glass.

Photolysis of $Mo(CO)_5(Tcp)$ and $W(CO)_5(P(OPr^i)_3)$ in MTHF Glass

As expected most of the bands in the spectra of both compounds are much broader in MTHF than in hydrocarbon solution and changes occur on cooling to 77K. The high frequency A_1 bands in both cases, however, remain very sharp and do not shift at all on cooling. In the $Mo(CO)_5(Tcp)$ case on cooling the B_2 mode becomes mode becomes quite distinct at 1978 cm^{-1}, the E band broadens slightly but does not shift from 1935 cm^{-1}, and the low frequency A_1 mode appears as a shoulder at 1918 cm^{-1}. In the $W(CO)_5(P(OPr^i)_3)$ case again the B_2 band becomes more clearly resolved although it is considerably shifted from 2000 cm^{-1} in hydrocarbon to 1982 cm^{-1}. The E band at 1937 cm^{-1} does not shift or show any major changes in shape, but the low frequency A_1 mode, which is resolved even at room temperature in hydrocarbon, only appears at 77K as a shoulder at 1945 cm^{-1} (a separation of 8 cm^{-1} between A_1 and E modes, cf. a separation of 13 cm^{-1} in hydrocarbon). These effects seem to be consistent with coordination of MTHF on the side of the molecule trans to the ligand.

In the $W(CO)_5(P(OPr^i)_3)$ case photolysis gives four new bands at 2021(m), 1900(m), 1885(vs), and 1842(s) cm^{-1}. Using WG 305 filtered light complete photolysis of starting material was achieved after 77 min. However, the concentration of the species responsible for these bands, probably cis-$W(CO)_4(P(OPr^i)_3)$(MTHF), did not increase after 30 min irradiation; so there must be complete decomposition taking place. As expected warm up to room temperature did not lead to regeneration of much starting material, but gave a spectrum with some cis-$W(CO)_4$ $(P(OPr^i)_3)$(MTHF) present and at least two other broad bands. The failure to observe trans-$W(CO)_4(P(OPr^i)_3)$(MTHF) can be explained in two ways (assuming that it is not present masked by the bands of the cis compound). If the main route to trans-$W(CO)_4(P(OPr^i)_3)$ is via the cis form, capture of the cis form by MTHF would prevent photoisomerisation, or trans-$W(CO)_4(P(OPr^i)_3)$ (MTHF) could be much more photosensitive than its cis analog and so decompose much faster.

In the $Mo(CO)_5$(Tcp) case seven new bands were observed on irradiation with WG 305 filtered light. More experiments would be required to identify all the bands, but it appears that cis-$Mo(CO)_4$(Tcp)(MTHF) (bands at 2015(m), 1895, 1885(vs), and 1845(s)) and fac-$Mo(CO)_3$(Tcp)$(MTHF)_2$ (bands at 1920(s), 1790(s), and 1775(s)) are present. Warm up to room temperature leads to almost complete regeneration of starting material.

$Mo(CO)_5$(Tcp) was also photolysed in 4:1 mch:ip containing 1% THF (i.e. about 0.07M in THF). Spectra before photolysis resemble those when THF was not present except that the E band showed a small splitting (1938, 1935 cm^{-1}) at 77K. Irradiation with WG 305 filtered light gave a mixture with cis-$Mo(CO)_4$(Tcp) (alkane) and cis-$Mo(CO)_4$(Tcp)(THF) as the main constituents.

<u>Photolysis of trans-$L_2M(CO)_4$ Compounds (L=$P(OEt)_3$, Tip, or PEt_3)</u>

Evidence for the loss of phosphine ligand from trans- $W(CO)_4$ $(Tip)_2$ during photolysis in solution at room temperature had previously been obtained in this department[24] and so it was decided to investigate this and similar species (trans-$Mo(CO)_4$ $(P(OEt)_3)_2$ and trans-$Cr(CO)_4(PEt_3)_2$) in glasses. Again photolysis via d--d transitions should lead to phosphine loss as a favoured process, but the favoured products of charge transfer photolysis are unknown. Another factor which should inhibit CO loss is the high electron density on a metal in a fragment such as $(PR_3)_2M(CO)_3$ which is bound to render it less stable than the corresponding $M(CO)_5$.

Trans-$M(CO)_4(PR_3)_2$ compounds show two or three i.r. bands, one very intense due to the i.r. allowed E_u mode and two much weaker at higher frequency due to A_{1g} and B_{2g} modes which are formally i.r. forbidden in D_{4h} symmetry. However, the molecules almost certainly undergo distortions similar to those described by Bigorne for trans-$Fe(CO)_4I_2$[154] ; so the actual symmetry is at most D_{2d}. The A_{1g} mode in D_{4h} correlates with the A_1 mode of D_{2d} which is also i.r. inactive and it is only in cases where there is interaction between the ligand and specific CO groups (i.e. where R=OEt etc.) that the 'A_{1g}' mode becomes i.r. active[21]. In the three cases investigated cooling of hydrocarbon solutions to 77K causes sharpening of all bands, including E_u. In the trans-$Mo(CO)_4(P(OEt)_3)_2$ case there is also an increase in intensity of both the high frequency bands relative to the E_u band. In all three cases the ^{13}CO band around 1845 cm^{-1} becomes better resolved on cooling and in the trans-$W(CO)_4(Tip)_2$ case a shoulder appears at 1915 cm^{-1} on the low frequency side of the B_2 (B_{2g}) band which is probably also due to a band of $W(CO)_3(^{13}CO)(Tip)_2$.

As expected photolysis with unfiltered light is very slow, the rate decreasing in the order $Mo(CO)_4(P(OEt)_3)_2 > Cr(CO)_4(PEt_3)_2 > W(CO)_4(Tip)_2$ i.e. the rate of photolysis is slower as the phosphine becomes more basic, although the metal is also changing. CO loss is the only observable photolytic reaction. The products show three i.r. bands which form a pattern typical of a T-shaped, C_{2v}, $L_2M(CO)_3$[83] or mer-$L_2L'M(CO)_3$[76] compound and are probably $(PR_3)_2M(CO)_3(alkane)_n$ compounds (see table 4-4).

<u>Table</u> <u>4-4</u>:

	trans-$Cr(CO)_4(PEt_3)_2$	trans-$Mo(CO)_4(P(OEt)_3)_2$	trans-$W(CO)_4(Tip)_2$
A_1 (A_{1g})	----	2041	----
B_2 (B_{2g})	1932	1970	1912
E (E_u)	1875	1915 1910	1855
	$Cr(CO)_3(PEt_3)_2$	$Mo(CO)_3(P(OEt)_3)_2$	$W(CO)_3(Tip)_2$
A_1	----	2000	1950
B_1	1841	1890	1836
A_1	1820	1842	1815

Trans-$W(CO)_4(Tip)_2$ was also photolysed in MTHF glass at 77K and MTHF solution at room temperature. Spectra of the starting material in MTHF glass were not much different from the corresponding spectra in hydrocarbon, but photolysis was very slow indeed, and after 3h irradiation with unfiltered light only one new band at 1828 cm^{-1} could be observed. However, irradiation at room temperature with unfiltered light caused the production of $W(CO)_5(Tip)$ and cis-$W(CO)_4(Tip)(MTHF)$, but after about 7 min a steady state was established (in a sealed cell) and further irradiation did not alter the composition of the mixture.

Norbornadienetetracarbonylchromium

Interest in the photolysis mechanism of this compound arose because it is thought to be involved in the hydrogenation reaction of norbornadiene in hexane at room temperature where irradiated $Cr(CO)_6$ is used as a catalyst[133]. One of the mechanisms suggested for this reaction, which is interesting because it gives more than the expected amount of 1,2 addition of H_2 to norbornadiene (NBD), involves a species in which NBD and H_2 are bonded to chromium simultaneously, possibly $Cr(CO)_3(NBD)(H_2)$. $Cr(CO)_6$ also catalyses a dimerisation reaction of NBD and $Cr(CO)_4(NBD)$ has been identified as an intermediate in that case[155], and $Cr(CO)_4$(diene) has been suggested as an intermediate in the $Cr(CO)_6$ photocatalysed hydrogenation of 1,3-dienes[156].

As with other substituted hexacarbonyls there are two possible decomposition routes, loss of CO or loss of ligand. In this case the second route is very unlikely in the glass as it would require simultaneous or consecutive detachment of both olefinic moieties from the metal and this is not likely to occur if no other two electron donors are free to move in to replace the olefin. Norbornadiene, however, absorbs in the near u.v. and so some of the light is bound to be absorbed by the ligand. This seems to have very little effect in the glass, although the photoassisted dimerisation of norbornadiene in the presence of $Cr(CO)_6$ probably involves such a process or a Cr to NBD charge transfer.

The i.r. spectrum of $Cr(CO)_4(NBD)$ at room temperature consists of four sharp bands at 2038(m), 1955(m), 1941(s), and 1910(s). On cooling the 1955 cm^{-1} band shifts to 1951 cm^{-1} and the 1910 cm^{-1} band to 1902 cm^{-1}, but the form of the spectrum changes little, except that when concentrations of over $5x10^{-3}$M are used broadening appears near the base of the two lowest frequency bands and the intensity of the other two bands is reduced. This is probably due to $Cr(CO)_4(NBD)$ coming out of solution, as, when concentrations of around 10^{-2}M are used, extensive crystallisation takes place. The two bands which shift on cooling, the low frequency A_1 and the B_2 are mainly due to motions of CO groups trans to the norbornadiene ligand.

Photolysis with unfiltered light is slower than photolysis of unsubstituted $Cr(CO)_6$, but not as slow as photolysis of $CpMn(CO)_3$. Free CO and five new i.r. bands are observed. On subsequent irradiation with WG 335 filtered light, three of the new bands at 1971, 1885, and 1873 cm^{-1} decrease in intensity while the other two at 1995 and 1918 cm^{-1} increase in intensity. There is also some regeneration of $Cr(CO)_4(NBD)$ and another band at 2078 cm^{-1} appears. After about 30 min irradiation with WG 335 filtered light a steady state is reached. The three bands at 1971, 1885, and 1873 cm^{-1} form a pattern which could well be due to (NBD)Cr$(CO)_3$(alkane) where an alkane molecule has substituted for one of the CO groups on the OC-Cr-CO axis, i.e. fac-Cr$(CO)_3$(NBD)(alkane), and the two bands 1995 and 1918 cm^{-1} could be due to the corresponding mer isomer, but many more experiments on this and related systems would be required to establish this. The origin of the 2078 cm^{-1} band, which is very weak, is unknown. Warm up to room temperature resulted in regeneration of about half the starting material and production of some Cr$(CO)_6$.

Photolysis experiments on Cr$(CO)_4$(NBD) and Cr$(CO)_6$ in the presence of NBD in H_2 saturated glass are currently in progress at Université Libre, Brussels and results of these experiments should relate to the above information. In particular, Cr$(CO)_3$(NBD)(H_2) should be formed in the photolysis of Cr$(CO)_4$ (NBD) and Cr$(CO)_4$(NBD)(H_2) may be formed in the photolysis of Cr$(CO)_6$ in the presence of NBD, and subsequent warm up reactions on these glasses may help to answer questions about the mechanism of the hydrogenation reactions.

Conclusion

Again this chapter can in no way be considered a systematic study of the photochemistry of substituted hexacarbonyls, but the information obtained shows the type of process which can occur in glasses , which are often different from the predominant processes in solution photochemistry. In fact the physical properties of the glass medium dominate the reactions described in this chapter. The structures inferred from spectra are necessarily speculative since no data from gas matrix studies on substituted hexacarbonyls is available yet, but in almost every case the spectra fit the structures expected if octahedral coordination about the metal is maintained in the CO deficient species.

The last section is an example of how photolysis in a glass followed by monitoring of spectral changes on warm up may be used as a model for a photocatalysis system. Unfortunately $Cr(CO)_6/NBD/H_2$ does not suit the method very well because of the low solubilities of $Cr(CO)_4(NBD)$ and H_2. It is important to remember that pre-photolytic association in the glass may change the primary reaction considerably from the reaction which occurs at room temperature.

CHAPTER 5

CYCLOPENTADIENYL MANGANESE TRICARBONYL AND RELATED COMPOUNDS

Introduction

$CpMn(CO)_3$ and its methylcyclopentadienyl analog ($MeCpMn(CO)_3$) are stable compounds which have been known since the early 1960's. They commonly undergo two types of reaction: substitution of CO groups[135] and Friedel-Crafts type, or possibly radical, additions to the cyclopentadiene ring[136]. They have also the possibility of coordination of two one electron donor ligands in place of CO[137] and form relatively stable dinitrogen substituted compounds[138].

Thermolysis of these compounds has been of interest because of their potential as catalysts --- $MeCpMn(CO)_3$ was tested as an anti-knock agent for petrol[139]. The photochemical reactions, however, tend to be relatively straight forward, leading to stepwise substitution of CO[135]. Like hexacarbonyls all the CO groups in the starting material are identical and so there is no possibility of more than one primary photolysis fragment being formed. The u.v./visible spectrum is dominated by a very intense u.v. absorption thought to be due to a cyclopentadiene ring transition[118], but there is at least one weaker band at longer wavelength which is probably a metal to CO charge transfer or d--d transition. The vibrational spectra of these compounds have also been studied extensively[140-142].

In this work $CpMn(CO)_3$ and $MeCpMn(CO)_3$ were photolysed in hydrocarbon and MTHF glasses at 77K. A few experiments in glasses with MTHF, CS_2, and CO_2 present were also carried out. The photolysis of $CpMn(CO)_2(CS)$ in hydrocarbon glass was also examined.

Photolysis in Hydrocarbon Glass

Like group VI hexacarbonyls $CpMn(CO)_3$ and $MeCpMn(CO)_3$ are relatively insoluble in 4:1 mch:ip and low concentrations ($\sim5\times10^{-3}M$) had to be used to avoid crystallisation on cooling. Higher concentrations could be isolated in mch:nujol mixtures (3:1 mch:nujol forms a glass around 160K). However, purification of nujol to remove aromatics to the extent required for this work was very difficult and so only a few experiments in 3:1 mch:nujol were carried out. The results in this medium are very similar to those obtained in 4:1 mch:ip.

Cooling to 77K in either 4:1 mch:ip or 3:1 mch:nujol shows changes in the i.r. spectra as expected. The very sharp A_1 band (2032 in $CpMn(CO)_3$) becomes sharper and shifts slightly to 2026 cm^{-1} while the E band (1946 cm^{-1} at room temperature) becomes broader and shifts to 1938 cm^{-1}. A weak band at 2020 cm^{-1} shows very little change in intensity, but another at 1913 cm^{-1} shifts to 1905 cm^{-1} and becomes slightly broader. A shoulder also develops on the low frequency side of the E band at 1924 cm^{-1}. These could be due to the three bands of $CpMn(CO)_2(^{13}CO)$ and the broadening of the lowest frequency band, which will be mainly due to ^{13}CO motion can be explained if ring rotation relative to CO groups is stopped in the glass so that there are three different stereoisomers of $CpMn(CO)_2(^{13}CO)$, two of which are enantiomers, and so the ^{13}CO group will be in two chemically different environments.(see fig. 5-1). This stopping

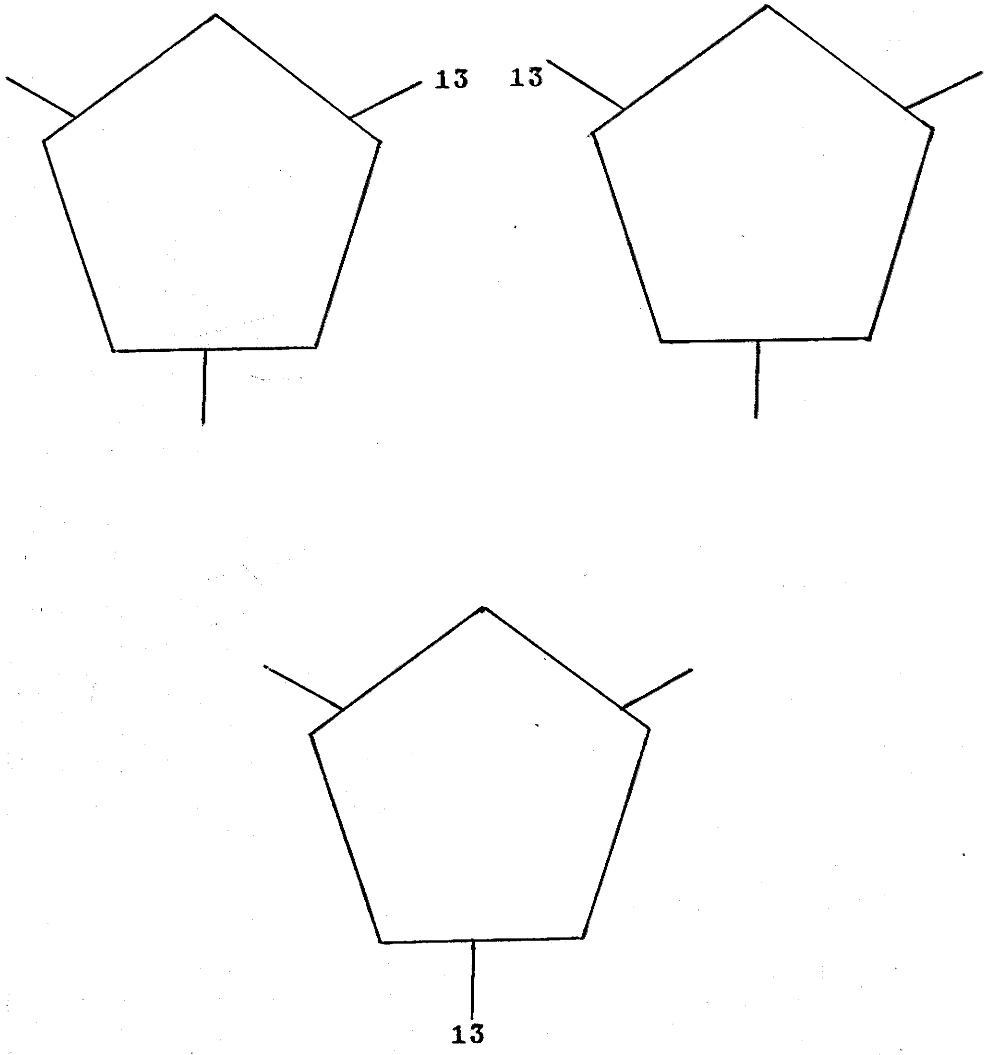


Figure 5-1: Possible rotamers of $CpMn(CO)_2(^{13}CO)$.

13= ^{13}CO

of ring rotation means that the effective symmetry of $CpMn(CO)_3$ molecules in the glass is C_s and so the E mode will be split into an A' and an A" component. This is consistent with the broadening observed. As expected these effects are more pronounced in $MeCpMn(CO)_3$ where more stereoisomers are possible, and in that case the A_1 band also shows some broadening on cooling.

Photolysis at 77K showed the usual stepwise loss of CO when light of wavelength <305 nm was used and photoreversal was observed on irradiation with lower energy (WG 335 filtered)light. Photolysis was relatively slow compared to the hexacarbonyls and complete photolysis of starting material was never achieved. The primary product showed two i.r. bands (see table 5-1) and is assigned as $CpMn(CO)_2$, although comparison with results in other matrices would be required to show whether it should be formulated as $CpMn(CO)_2$(alkane). Because of the persistence of the starting material no visible spectra could be obtained.

Since both $CpMn(CO)_3$ and $CpMn(CO)_2$ contain only one type of CO group, C-M-C bond angle calculations from band intensities are fairly simple[95] and the results are shown in table 5-1. The values obtained for $CpMn(CO)_3$ (94-96°) are close to the values of 91, 91, and 94° found in the crystal[141]. Relative band intensities were measured in the same way as for $Mo(CO)_4$ by measuring peak height on a logarithmic scale and multiplying by FWHM. Although no corrections for intensity in the wings of the bands were made and the dipole moment derivative

Table 5-1: CO stretching frequencies of $CpMn(CO)_3$, $MeCpMn(CO)_3$, and primary photolysis products in hydrocarbon glass at 77K.

Compound	CO stretching frequency		K	k_i	$C-\widehat{Mn}-C$
	symmetric	antisymmetric			
$CpMn(CO)_3$	2026	1938	15.64	0.470	94°
$MeCpMn(CO)_3$	2022	1936	15.59	0.460	98°
$CpMn(CO)_2$	1955	1886	14.90	0.535	100°
$MeCpMn(CO)_2$	1950	1881	14.82	0.530	110°

K, k_i units md/A

K CO stretching force constant

k_i interaction constant

was assumed to be the same under all vibrations, the values for $CpMn(CO)_3$ are close enough to the crystal structure values to suggest that the increase in angle between $CpMn(CO)_3$ and $CpMn(CO)_2$ of 4-6° may be significant.

It is impossible to tell from two i.r. bands whether $CpMn(CO)_2$ has a structure with the cyclopentadiene ring perpendicular to the OC-Mn-CO plane. This might be expected if the species observed is truly $CpMn(CO)_2$ since $CpCo(CO)_2$ is thought to have this type of structure[144]. However, a $CpMn(CO)_2$ (alkane) species would probably have a structure similar to $CpMn(CO)_2L$ compounds in which the ring is not perpendicular to the OC-Mn-CO plane[158]. A similar bond angle calculation on $CpCo(CO)_2$ in mch solution at room temperature gave a $C\widehat{Co}C$ angle of 84° (temperature was found to make little difference to the relative intensities in $CpMn(CO)_3$) and so $CpMn(CO)_2$ in hydrocarbon may well have a $CpMn(CO)_2L$ type structure.

Prolonged photolysis (>80 min with unfiltered radiation) produced a further band at 1857 cm^{-1} in the $CpMn(CO)_3$ case and 1856 cm^{-1} in $MeCpMn(CO)_3$. Although it is conceivable that $CpMn(CO)(^{13}CO)$ could have a band at this frequency, in the $MeCpMn(CO)_3$ case at least, the observed band is much stronger than 2% of the A" (or B_1) band of $MeCpMn(CO)_2$, and so is probably due to $MeCpMn(CO)$.

Prolonged irradiation also produces two weak bands at 1967.5 and 1910 cm^{-1} in the $MeCpMn(CO)_3$ case and 1970 and 1917

cm^{-1} in the $CpMn(CO)_3$ case. These may well be due to impurities in the glass since they were observed in 3:1 mch:nujol and nujol is extremely difficult to purify to remove traces of aromatics and olefinics. $CpMn(CO)_2$(olefin) compounds have bands around 1975 and 1920-1910 cm^{-1} [145]. $MeCpMn(CO)_3$ irradiated at room temperature in Apiezon L or N grease, which both contain some u.v. absorbing impurities -- probably aromatics, shows bands at 1960 and 1898 cm^{-1} in addition to the bands at 1944 and 1877 cm^{-1} assigned to a $MeCpMn(CO)_2$ type species, possibly $MeCpMn(CO)_2$(grease molecule). On prolonged photolysis in greases (>30 min, unfiltered light) shoulders develop on the low frequency side of both '$MeCpMn(CO)_2$' bands at 1933 and 1870 cm^{-1}.

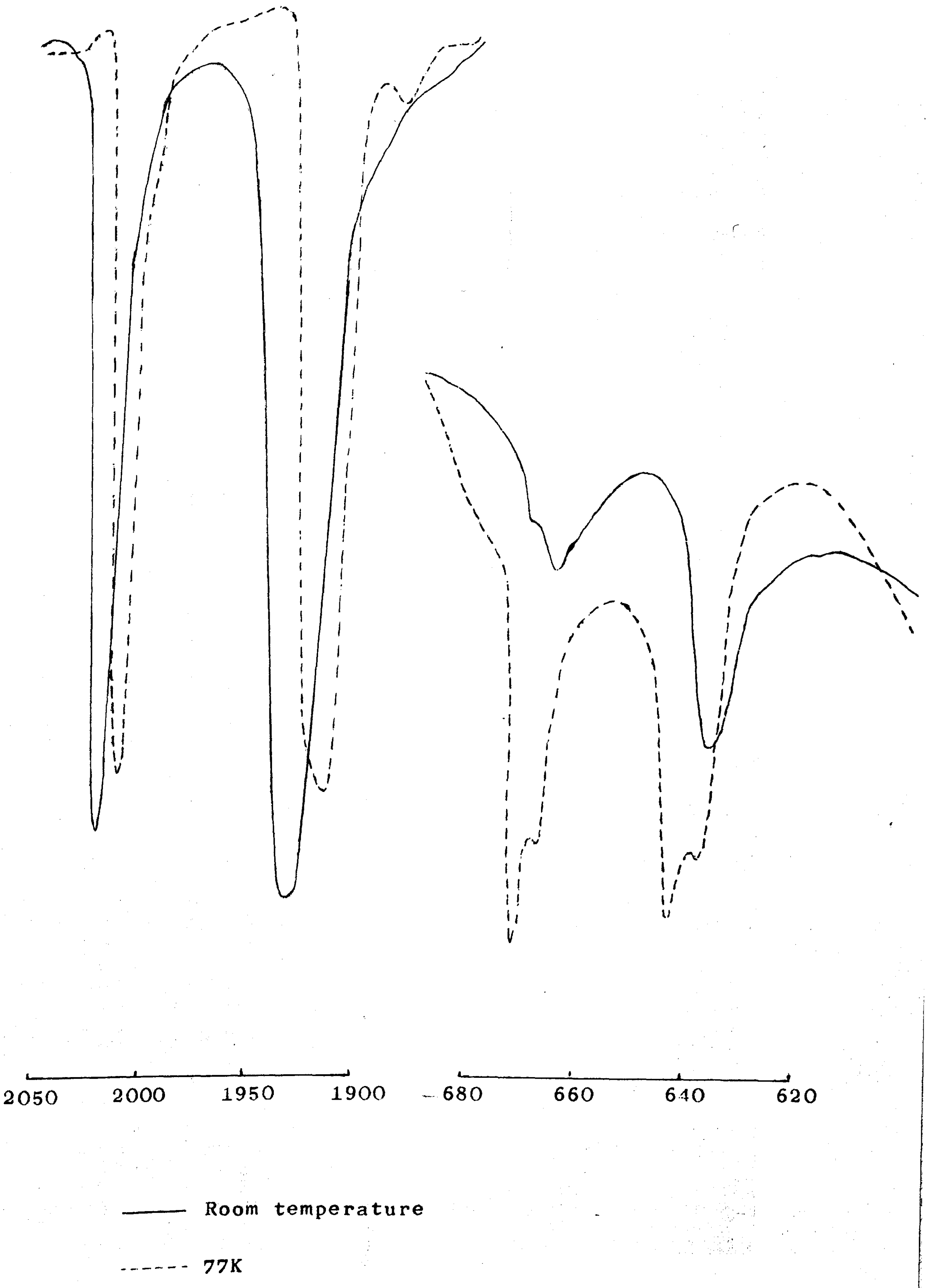
These last results are in contrast to those obtained for $Mo(CO)_6$ irradiated in Apiezon grease where the main product, on irradiation with WG 335 filtered light, appeared to be $Mo(CO)_5(H_2O)$. A possible experiment, which was not carried out, would be photolysis of $Mo(CO)_6$ in rigorously dried (over Na at high temperature, say) Apiezon grease. 'Solutions' of $Mo(CO)_6$ in grease were prepared by mixing a solution of $Mo(CO)_6$ in ip with the grease and pumping on the resulting sludge for several days to obtain a fairly hard grease. The results in the $Mo(CO)_6$ case were irreproducible because of varying grease hardness or varying water content. In the $MeCpMn(CO)_3$ case the liquid was simply dissolved in molten grease at about 50°C.

Warm up experiments on samples of $CpMn(CO)_2$ in the absence of impurity complexes in 3:1 mch:nujol showed disappearance of $CpMn(CO)_2$ and regeneration of starting material around 170K. The glass forming mixture used had the consistency of a soft grease (e.g. Kel-F) at 195K. These results cannot be directly compared with the results of warm up experiments in the hexacarbonyl and $Fe(CO)_5$ cases, but it seems that $CpMn(CO)_2$ in hydrocarbon is considerably less reactive than $M(CO)_5$ or $Fe(CO)_4$ in hydrocarbon and that it does not coordinate water or form polymers easily. It is also interesting to note that $CpMn(CO)_2(N_2)$ which can be isolated at room temperature[138] was not observed during glass warm up experiments.

Photolysis in Methyltetrahydrofuran Glass

As with the other systems investigated cooling to 77K caused considerable changes in the $CpMn(CO)_3$/MTHF i.r. spectrum. In the CO stretching region the A_1 band shifts from 2021 cm^{-1} at room temperature to 2011 cm^{-1} and the E mode shifts from 1932 to 1915 cm^{-1} (see fig. 5-2). These shifts occur gradually on cooling and are reversible on warm up. The width of the A_1 band does not change much, but the E band shows a similar type of incipient splitting to that observed for the E' band of $Fe(CO)_5$. A weak band also appears at 1885 cm^{-1} which may be due to $CpMn(CO)_2(^{13}CO)$ since a corresponding band is observed at 1905 cm^{-1} in hydrocarbon glass. The shifts of 10 and 17 cm^{-1} in the A_1 and E modes respectively show that there must be considerable interaction between MTHF and $CpMn(CO)_3$ on cooling.

Figure 5-2: $CpMn(CO)_3$ in MTHF room temperature and 77K.



and the frequencies of 2021 and 1932 cm^{-1} in the room temperature spectrum indicate that there is interaction with MTHF even at that temperature (cf. 2032 and 1942 cm^{-1} in hydrocarbon).

In the δM-C-O region the spectrum of CpMn(CO)$_3$ in MTHF at room temperature shows a band at 665 cm^{-1} with a shoulder on the high frequency side at 671 cm^{-1} and another band at 636 cm^{-1}. Both are fairly broad and about one fifth as intense as the E CO stretching band and are assigned to A$_1$ and E δM-C-O motions[142]. The origin of the 671 cm^{-1} shoulder is not clear, but the 665 cm^{-1} band is assigned to an A$_1$ mode as it is close to a polarised Raman band at 670 cm^{-1} [140]. On cooling the two bands gradually sharpen, but around 170K major changes begin to take place and by 108K the 672 cm^{-1} component of the higher frequency band becomes the more intense, while the low frequency band splits into two components at 643 and 638 cm^{-1} (fig. 5-2).

The effects observed in both regions of the spectrum are consistent with coordination of MTHF either to the metal or to a CO group. The lowering of both CO stretching frequencies, which is much more dramatic than the corresponding effect in Fe(CO)$_5$ or M(CO)$_6$ in MTHF, suggests that coordination is probably to the metal. Compounds with four other ligands and cyclopentadiene bonded to manganese (as Mn(II)) are well known (see ref. 138 and references therein), and coordination of a basic ether to Mn would be expected to increase the electron density on the Mn and so cause a lowering of both CO stretching frequencies. A $CpMn(CO)_3(MTHF)$ compound will have a maximum symmetry of C_s and three i.r. active CO stretches, two of which correlate to the E mode of $CpMn(CO)_3$ and are probably similar in frequency to it. In the δM-C-O region the E mode at 636 cm^{-1} will also be split into A' and A" components (643, 638 cm^{-1}). The A_1 mode at 665 cm^{-1} will correlate directly with an A' mode (668 cm^{-1}) and the inactive A_2 mode correlates with an A" mode which is probably responsible for the band at 672 cm^{-1}. The shoulder at 671 cm^{-1} in the room temperature spectrum may well be due to the A_2 mode being weakly activated by coordination of MTHF or it may be due to the corresponding A" mode of $CpMn(CO)_2(^{13}CO)$. Adams and Squire[140] observed a band around 670 cm^{-1} in i.r. spectra of solid $CpMn(CO)_3$ and in spectra in CS_2 and C_2Cl_4 solution, but did not comment on its origin. $MeCpMn(CO)_3$ in MTHF showed similar changes in the spectrum, in the CO stretching region at least.

Photolysis of $CpMn(CO)_3(MTHF)$ would be expected to give $CpMn(CO)_2(MTHF)$ and CO as primary products. However, irradiation at 77K with unfiltered or WG 305 filtered light produced four new bands, the frequencies of which are listed in table 5-2. The same four bands were produced in apparently the same relative intensities over a range of concentration of starting material from 5×10^{-3}M to 0.1M. A similar set of bands were also observed for $MeCpMn(CO)_3$ in MTHF after photolysis. The relative intensities of the bands are impossible to measure in

Table 5-2: Frequencies of $CpMn(CO)_3$ and $MeCpMn(CO)_3$ and primary photolysis products in MTHF and 4:1 mch:ip+5% THF.

Compound		MTHF		4:1 mch:ip+5% THF	
		293K	77K	293K	77K
$CpMn(CO)_3$	A_1	2021	2011	2032	2021
	E	1932	1915	1948	1922
$CpMn(CO)_2L$	A'	1925	1942 1919	----	1942 1916
	A"	1851	1870 1840	----	1865 1834
$MeCpMn(CO)_3$	A_1	2020	2015		
	E	1939	1927		
$MeCpMn(CO)_2L$	A'	----*	1937 1915		
	A"	1850	1866 1836		

* band masked by E band of parent.

pure MTHF because of overlap of the new bands and overlap of the bands around 1930 cm^{-1} with the E band of the parent tricarbonyl.

Photolysis was very slow compared to $M(CO)_6$/MTHF and $Fe(CO)_5$/MTHF systems and irradiation times of around 3h still did not produce complete photolysis of starting material. Photoreversal was not observed. The low rate of photolysis may be due to u.v. absorption by the very intense cyclopentadienyl ring transitions which do not lead to CO loss.

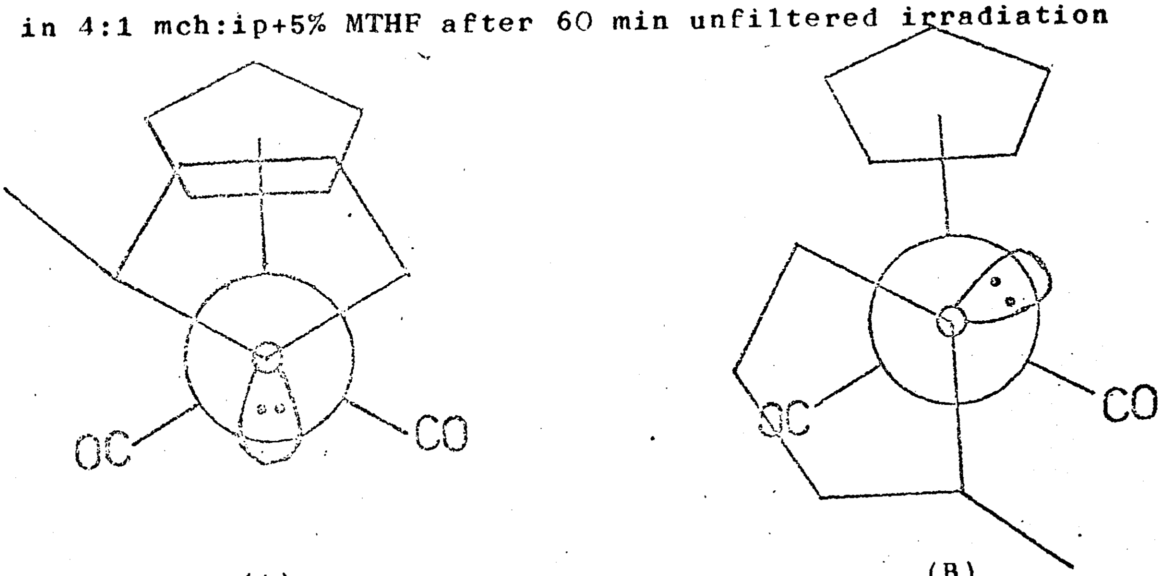
Experiments in mixed 4:1 mch:ip/THF and 4:1 mch:ip/MTHF glasses showed similar effects in the CO stretching region on cooling, but the shifts observed are less than those observed in pure MTHF (see table 5-2). Again photolysis with unfiltered or WG 305 filtered light produces four new bands in similar relative intensities to those observed in pure MTHF. Surprisingly photolysis was faster than in pure MTHF and complete photolysis could be achieved after about 90 min irradiation with unfiltered light. In the THF case a further band at 1768 cm^{-1} due to a secondary photolysis product was observed.

Two band patterns of the type expected for $CpMn(CO)_2L$ compounds are observed on photolysis of $CpMn(CO)_3$ or $MeCpMn(CO)_3$ in THF, MTHF, or hydrocarbon solutions of these at room temperature or 195K, and, on glass softening, the four bands observed in the glass collapse to similar two band patterns. These observations can be explained if the species generated by primary photolysis is in fact $CpMn(CO)_2(MTHF)$, but rotation about the Mn-O bond is restricted in the glass. Restricted rotation about the Mn-S bond in $CpMn(CO)_2(THT)$ (THT= tetrahydrothiophene) has been observed by Butler in solution spectra and the barrier to rotation has been estimated at around 0.8 Kcal/mole[146]. However, it seems that in this case rotation about the Mn-O bond is virtually free at 100K and that it is only hindered at 77K by the rigidity of the glass medium.

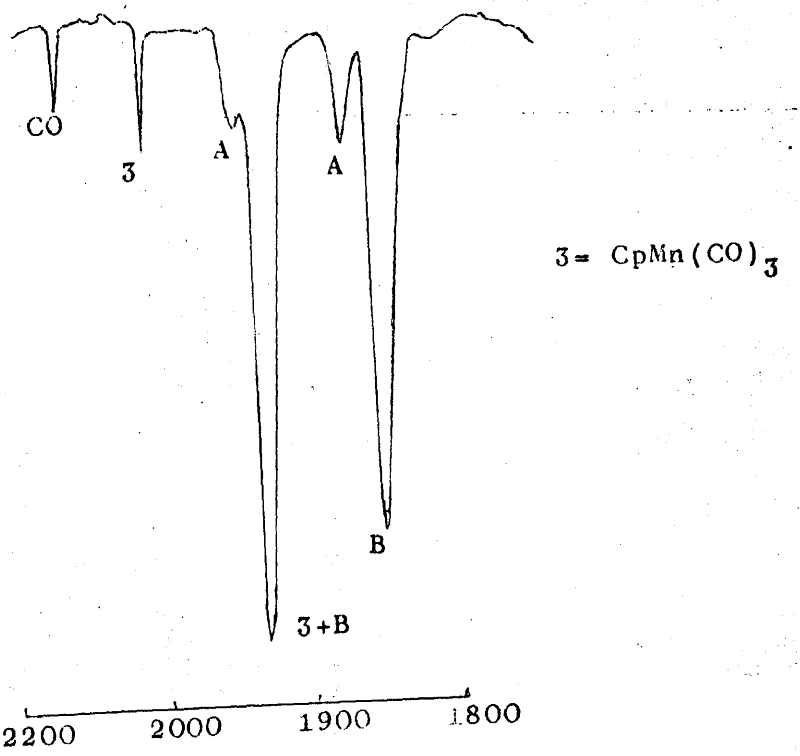
As can be seen from the spectra (fig. 5-3) there is one preferred rotamer and another minor form. The preferred form is probably isomer (B) (see fig. 5-3) which is less sterically hindered. In $CpMn(CO)_2$(thioether) complexes Butler assigned the lower frequency, more intense set of bands to an isomer similar to (B) on the basis of the results of experiments with $C^{18}O$ substituted molecules[146]. The fact that the high energy conformer is not converted to the more stable form on prolonged photolysis or irradiation with low energy light is consistent with Burdett's view that local lattice softening does not take place during photoreversal[27]. There is, however, a considerable difference in the frequency splittings between isomers observed here (between 20 and 30 cm^{-1}) and those observed by Butler for $CpMn(CO)_2$(thioether) (between 7 and 10 cm^{-1}) and so it is possible that the two types of isomerism are not analogous.

The difference in behaviour of $CpMn(CO)_3$/THF in 4:1 mch:ip

Figure 5-3: Rotamers of $CpMn(CO)_2(MTHF)$ and spectrum of $CpMn(CO)_3$ in 4:1 mch:ip+5% MTHF after 60 min unfiltered irradiation



(A)　(B)



from the other systems supports the view that the isomerism is rotational. In that case the bands of the less favoured isomer, especially the higher frequency band, are much broader than the corresponding bands in MeCpMn$(CO)_3$/THF and the MTHF systems, probably because they are composites of several bands belonging to a range of rotamers, i.e. rotation is less hindered in that case, but there is still a preferred form. In 4:1 mch:ip containing 5% THF (i.e. around 0.4M in THF) there is evidence for association of a second THF with CpMn$(CO)_3$(THF) since, even after 30 min irradiation at 77K, CpMn(CO)$(THF)_2$ (band at 1768 cm^{-1}) is observed, and the high frequency bands of the two isomers observed at 77K (1942, 1916 cm^{-1}) are much lower than the corresponding band observed at room temperature. In CpMn$(CO)_3$/MTHF in 4:1 mch:ip at 195K the corresponding band was observed at 1925 cm^{-1}, probably indicating coordination of a second MTHF to CpMn$(CO)_2$(MTHF). However, further substitution of CO was not observed in this case, presumably because formation of CpMn(CO)$(MTHF)_2$ would be difficult for steric reasons.

Another possible reason for the appearance of two extra bands on photolysis in the glass is that there is interaction of CpMn$(CO)_2$(MTHF) etc. with ejected CO and that the new bands are due to CpMn$(CO)_2$(MTHF)...CO. This is unlikely, however, since the two bands in question disappear around 90K when there is still a band due to uncoordinated CO visible, and the bands reappear on cooling to 77K. It is not clear whether the changes in spectra occurring on warming from 77 to 90K are truly reversible since the bands due to the less favoured isomer of $CpMn(CO)_2(MTHF)$ etc. are very weak. To determine whether the changes are completely reversible spectra would have to be run on a spectrometer with better resolution and facilities for ordinate expansion so that meaningful relative intensities could be estimated. (This work was carried out on a PE 457.)

Photolysis in the Presence of Other Potential Ligands

$CpMn(CO)_3$ was photolysed in hydrocarbon glass in the presence of CS_2 and CO_2.

(A) Carbon Disulphide: As was mentioned earlier $CpMn(CO)_2(CS_2)$ is thought to be an intermediate in the formation of $CpMn(CO)_2(CS)$ from $CpMn(CO)_2$(olefin) in CS_2 solution[126], where the reaction is thought to be initiated by loss of olefin to give $CpMn(CO)_2$. Thus it is likely that if the species generated by photolysis in hydrocarbon is in fact $CpMn(CO)_2$ a similar $CpMn(CO)_2(CS_2)$ compound would be formed by photolysis in the presence of CS_2.

$CpMn(CO)_3$ was photolysed in 4:1 mch:ip containing 10% CS_2 (by volume) (i.e. approx 1M in CS_2; approx 10^{-2}M in $CpMn(CO)_3$). On cooling to 77K the bands in the spectrum showed the expected broadening due to pre-photolytic interaction, although the frequencies observed, 2027 (A_1) and 1938 (E), were similar to those observed in the absence of CS_2. An expanded spectrum showed that both bands were asymmetric after cooling, indicating that there must be more than one species present. Photolysis with unfiltered light for 60 min followed by photolysis with WG 305 filtered light for 60 min showed production of a small amount of CO together with a reduction in intensity of the tricarbonyl bands and a slight shift of the E band to 1935 cm^{-1}. A very weak band was also observed at 2045 cm^{-1} and there was a slight reduction in intensity of the CS_2 overtone band observed at 2179 cm^{-1}. Incidentally, this band at room temperature is considerably broader with a shoulder on the low frequency side, probably because the CS_2 is rotating in solution causing the S-C-S stretching band and its overtones to have P-R branch structures. In the glass, however, rotation is not possible. During warm up a shoulder developed on the low frequency side of the $CpMn(CO)_3$ band at 2021 cm^{-1} and at least two broad bands appeared in the 1930-1900 cm^{-1} region. These changes occurred gradually between 100 and 165K. Above this temperature all bands except those of the parent tricarbonyl gradually disappeared, but by no means all of the $CpMn(CO)_3$ in solution was regenerated on warm up to room temperature.

$CpMn(CO)_2(CS_2)$ was possibly generated in this experiment, but there was no positive evidence for its existence. The 2045 cm^{-1} band is at a high frequency for a CO stretch in a neutral $CpMn(CO)_3$ derivative and could well be due to coordinated CS_2. The warm up experiments were probably confused by $CpMn(CO)_3$ coming out of solution. However, there was also no evidence for the formation of $CpMn(CO)_2$ (or $CpMn(CO)_2$(alkane)) in this system.

(B) Carbon Dioxide: $CpMn(CO)_3$ was photolysed in the presence of both wet and dry CO_2. The results were different in each case and the 'wet' system will be discussed first. A degassed solution of $CpMn(CO)_3$ (about 10^{-3}M, in 4:1 mch:ip) was added to card-ice and a sample of the resulting CO_2 saturated solution was removed at about 0°C and transferred to a sealed VLT-2 cell. At room temperature the spectrum showed a CO_2 stretching band at 2340 cm^{-1} and the normal $CpMn(CO)_3$ spectrum. On cooling to 77K the CO_2 band sharpened slightly and shifted to 2342 cm^{-1} and a $^{13}CO_2$ band at 2282 cm^{-1} became visible, while the A_1 band of $CpMn(CO)_3$ shifted to 2025 cm^{-1} and became slightly broader and the E band shifted to 1922 cm^{-1} and became broad and flat topped. Irradiation with unfiltered light caused production of CO, a shift of the top of the 'E' band to 1915 cm^{-1}, and the appearance of a new band at 1835 cm^{-1}. Warm up experiments showed a tremendous increase in the intensity of the 1835 cm^{-1} band around 123K, but by 165K it had almost disappeared. A band at 1722 cm^{-1} was also observed around this temperature, although it may have been present at lower temperatures. Around 165K the $CpMn(CO)_3$ bands were considerably broader than at 77K and on farther warm up showed a gradual sharpening until by about 250K they were as sharp as at room temperature. However, there was a shoulder on the low frequency side of the E band at 1935 cm^{-1} and the 1835 cm^{-1} band (which had shifted to 1817 cm^{-1} by room temperature) and the 1722 cm^{-1} band persisted at room temperature, and there was by no means complete regeneration of $CpMn(CO)_3$.

The 1835 and 1722 cm^{-1} bands also sharpened considerably on warm up.

From the effect of cooling on the CpMn(CO)$_3$ bands there is obviously association of either CO$_2$ or water or both on cooling, and it appears that loss of CO from CpMn(CO)$_3$ is a photoreaction taking place in the glass. CO$_2$ does not absorb in the near u.v.; so photoreactions of CO$_2$ with solvent are unlikely. 1835 cm^{-1} is around the frequency expected for a C=O absorption in carbonic acid. This, however, could not be observed in the i.r. spectrum of CO$_2$ in aqueous solution at room temperature[147]. 1722 cm^{-1} on the other hand is a frequency typical of a ketonic C=O absorption. There many possibilities for the reactions which may be taking place, e.g. CO$_2$ could be reacting with H$_2$O to give carbonic acid at a CpMn(CO)$_2$ centre, or CO$_2$ could be substituting into the cyclopentadiene ring. Both these processes would be consistent with a first step of coordination of CO$_2$ to CpMn(CO)$_2$ through CO$_2$ oxygen, thus making the CO$_2$ more acidic at carbon.

The reactions observed using CO$_2$ from a cylinder dried by passing through a P$_2$O$_5$ column and handling solutions away from air were different. The room temperature spectrum of the starting solution was similar, but on cooling to 77K the CO$_2$ band split into two components at 2355 and 2342 cm^{-1} and although the E band of CpMn(CO)$_3$ was broadened it had a considerably different shape from the corresponding spectrum in the wet CO$_2$

case. Irradiation for 75 min with unfiltered light produced bands similar to those of $CpMn(CO)_2$ produced in hydrocarbon in the absence of CO_2 (1955 and 1886 cm^{-1}) and two new bands in the CO_2 region at 2362 and 2290 cm^{-1}. As in the case of wet CO_2 the system is not yet understood and many more experiments are necessary. However, any system in which CO_2 is modified photochemically, through coordination to a photolysis fragment or otherwise, is potentially interesting.

Cyclopentadienyl Manganesedicarbonylthiocarbonyl

A sample of $CpMn(CO)_2(CS)$ (provided by I.S. Butler) was photolysed in 4:1 mch:ip. It was thought that this compound would show stepwise loss of CO to give CpMn(CO)(CS) and CpMn(CS) since CS is a better π acceptor and also heavier than CO. A solution of 1.1×10^{-2}M $CpMn(CO)_2(CS)$ showed two i.r. bands at 2010 and 1962 cm^{-1} which shifted to 2008 and 1955 cm^{-1} on freezing to 77K. On irradiation with unfiltered light one new band at 1940 cm^{-1}, presumably due to CpMn(CO)(CS), and CO were produced. Fast warm up to +30°C (over about 10 min) did not show complete regeneration of starting material, and showed a weak band at 1995 cm^{-1} which is the frequency of the CO stretch in $CpMn(CO)(CS)_2$[126].

Conclusion

As in the other systems investigated the predominant photochemical reaction of $CpMn(CO)_3$ in glasses is CO loss. It might be expected that there would be less relation between this behaviour and the behaviour in room temperature solution photochemistry than there is in other, all carbonyl, systems because of the possibility of reactions of the cyclopentadiene ring since ring transitions are important in the u.v. spectrum. However, the room temperature work in greases shows that the same processes can take place at room temperature, and the results of preparative chemistry (e.g. ref. 135 and references therein) show that they almost certainly do. Irradiation in the presence of MTHF, CS_2, and CO_2 showed that similar association of carbonyl and potential ligand to that observed in hexacarbonyls and $Fe(CO)_5$ can take place, and the magnitude of the shifts in the MTHF case shows that the strength of the association is probably greater in this case. There is still room, however, for a systematic study of the photolysis reactions of $CpMn(CO)_3$ in the presence of potential ligands, and the reaction in the presence of CO_2, wet and dry, should be investigated further.

APPENDIX

EXPERIMENTAL TECHNIQUES

Introduction

The glass photolysis experiment obviously needs specialist apparatus different from anything commonly used in preparative chemistry or room temperature spectroscopy. A basic technique had been evolved by M.J. Boylan in this department using modifications of commercial apparatus and this technique was further developed in the course of this work. Details of various aspects are described in sections B to E of this chapter.

Experiments were always conducted on a very small scale (as little as $5x10^{-7}$ moles of starting material being used) and the concentrations of solutions used to form glasses ($\sim 10^{-2}M$) was of the same order as the concentration of impurities in commercial 'pure' (e.g. Analar grade) solvents, and also of the same order as the solubilities of N_2 and O_2 in hydrocarbon solvents at atmospheric pressure[50]. Fortunately, not all the impurities in the solvents affected the reactions. For example the methylcyclohexane used contained up to 1% n-heptane (from g.l.c. results), but addition of more heptane did not seem to affect photolysis results, and although nitrogen must have been present in almost all the glasses used no N_2 complexes were detected. However, some impurities had to be removed, e.g. toluene from methylcyclohexane. Often impurities had no effect on reactions in the glass because the chances of an impurity molecule and a molecule under examination being trapped in the same site in the glass are very small unless there is some interaction between them in the solution before freezing, but impurities became apparent when they interfered with reactions during warm up. An example of this was observed when traces of water, which are almost impossible to remove from stainless steel apparatus, reacted with group VI pentacarbonyl fragments after glass softening. Details of purification proceedures are given in section A.

The following sections A to E outline the general experimental proceedure used in this work. Where specific techniques were employed to overcome problems of a particular experiment, they are described in detail in the chapters where the results of the experiments are discussed.

A) Preparations and Purification of Reagents

i) Hexacarbonyls: Hexacarbonyls of chromium, molybdenum, and tungsten were obtained commercially and were normally used without further purification. On some occasions these materials were vacuum sublimed before use, but this was found to have no effect on their spectra or the photolysis results.

ii) Pentacarbonyl iron: Solutions of $Fe(CO)_5$ were made up by distilling commercial $Fe(CO)_5$ into the chosen solvent on a vacuum line. Concentrations were estimated by i.r. and the solutions were stored in a refrigerator at 0^oC until use.

iii) Cyclopentadienyl manganese tricarbonyl: $CpMn(CO)_3$ was purified by vacuum sublimation before use: commercial $MeCpMn(CO)_3$ was used without farther purification.

iv) Monosubstituted hexacarbonyls: A number of standard methods are available for the preparation of these[21,51,52], and preparation was normally carried out on a 0.1g scale by the indirect method of treating the pentacarbonylchloride anion with the chosen ligand and aluminium trichloride in methylene chloride solution[52]. This method was found to be the most convenient on the small scale used, but direct thermal methods[21] were found to give better yields on a larger (2g) scale. Pentacarbonylchloride anions were prepared as their tetraethylammonium salts from the hexacarbonyls by the method of Abel et al.[53] The indirect photochemical method using a THF complex as intermediate[51] was not found to be particularly successful, producing a crude product which was contaminated with large amounts of starting hexacarbonyl, the removal of which was very time consuming. Purification of the product was usually achieved by chromatography on an alumina column (30 cm x2 cm) using 40-60 pet.-ether as eluant, except in the case of trihalophosphine complexes where vacuum sublimation was used. The purity of the products was checked by i.r. and the complexes were usually photolysed immediately after purification. Complexes which were stored were kept in a refrigerator at 0°C, or under dry nitrogen in the case of halophosphine ligands.

v) Disubstituted hexacarbonyls: These were prepared by thermal reactions according to the methods of Milne[21]. Purification again was by chromatography on alumina using pet.-ether as eluant.

vi) 2-methyltetrahydrofuran (MTHF): MTHF and THF were distilled off CaH_2 under dry nitrogen and stored under nitrogen until use or distilled off potassium with benzophenone present as a moisture indicator. The latter method was not used for MTHF which would be used as glass forming solvent because of the danger of contamination of the distillate with benzophenone.

vii) Hydrocarbon solvents: Methylcyclohexane and isopentane were stirred over conc. sulphuric acid for several days to remove aromatics, and were then washed with water, sodium carbonate solution, and water again and dried over $MgSO_4$ before being passed through a silica gel column to remove traces of olefinics and stored over $MgSO_4$. Purity was checked using u.v. spectroscopy. When particularly dry solvent was required, it was distilled off fresh Na wire on a vacuum line.

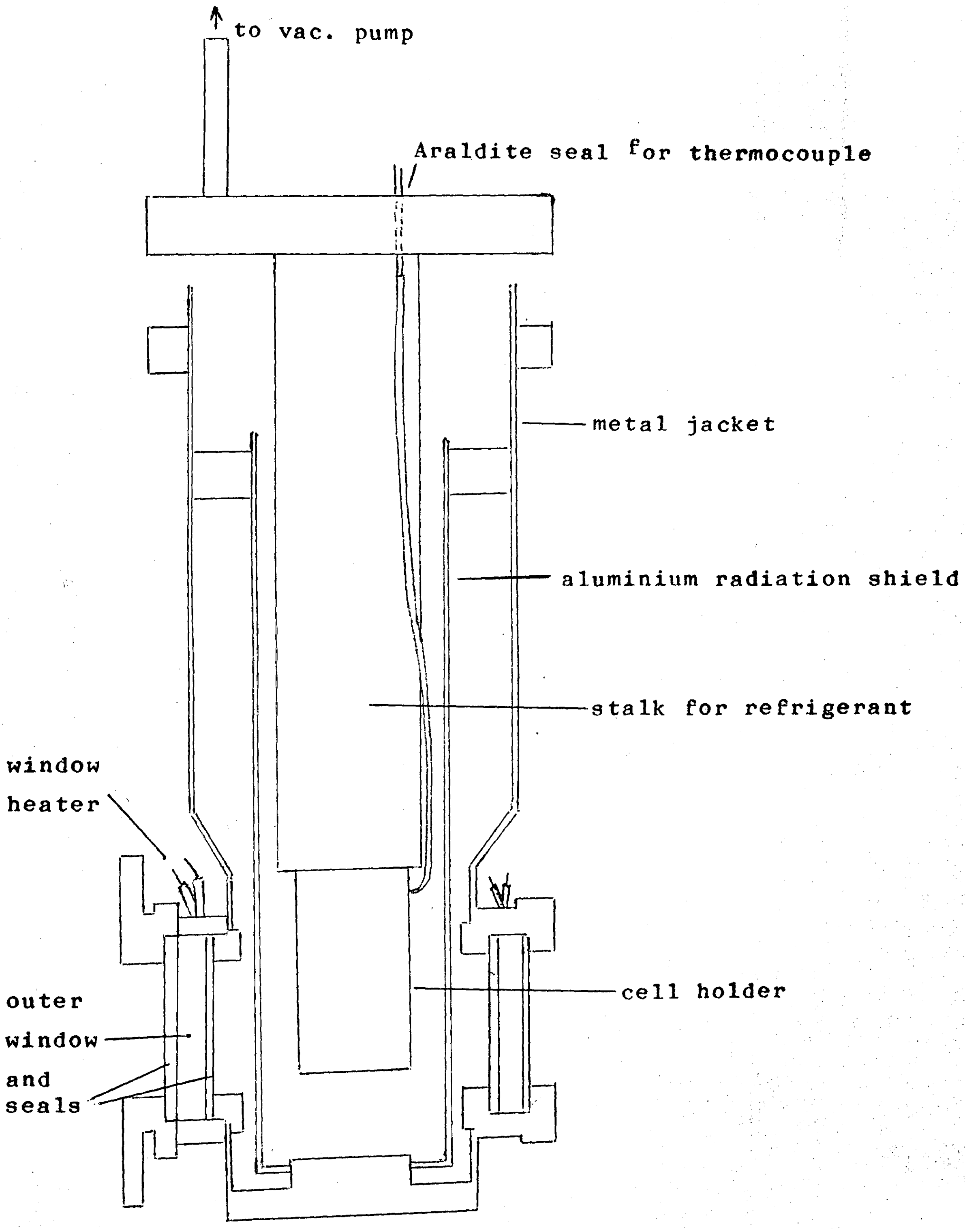
viii) Carbon disulphide: Copper dust was used to remove inorganic sulphides, and then CS_2 was distilled under nitrogen.

ix) Phosphine ligands: Liquid phosphines were redistilled under vacuum before use. Commercial $P(p\text{-}C_6H_4CH_3)_3$ was used without further purification. Tricyclohexylphosphine was recrystallised from a pentane-toluene mixture under a nitrogen atmosphere and stored under dry nitrogen. Bromo and chlorophosphines were found to react with or dissolve every grease available (silicone, Apiezon L,N, 101, and Kel-F) and so Kel-F wax was used. However, this still reacts slowly with these compounds.

B) Low Temperature Cell Construction

Most reactions were carried out by photolysis of a glass in situ in an i.r. cell. The apparatus most commonly used was a Beckmann-RIIC VLT-2 variable temperature i.r. cell with a few modifications. This consists of a sealed solution cell on the end of a hollow metal stalk which is encased in a metal jacket which can be evacuated (fig. A-1). Cooling is achieved by pouring refrigerant into the metal stalk. Thermocouples were made from chromel and alumel wire and calibrated with ice, solid CO_2, and liquid N_2, and the temperature was monitored using these in conjunction with a Beckmann TEM-1C temperature controller. Liquid nitrogen was the normal refrigerant used and it was found that the thermocouple (in direct contact with the metal part of the sample cell) would register a temperature of 77K within 10 min of cooling beginning. The electric cell heaters supplied with the VLT-2 were found to be completely inadequate (at least around 77K) and were removed. A reproducible, though not a linear rate of warm up could be obtained simply by emptying the liquid nitrogen out of the stalk. This gave an initial rate of warming of about 5 deg min^{-1}, but this gradually slowed until room temperature was reached after about 65 min. Very fast warm up (~3 min) could be achieved by a flow of hot water through the stalk. The main disadvantage of the VLT-2 was the tendency to develop leaks in the seals between the stalk and the jacket and between the jacket and the outer windows causing misting of the inner cell windows during long

Figure A-1: Diagram of VLT-2 jacket and cell holder.

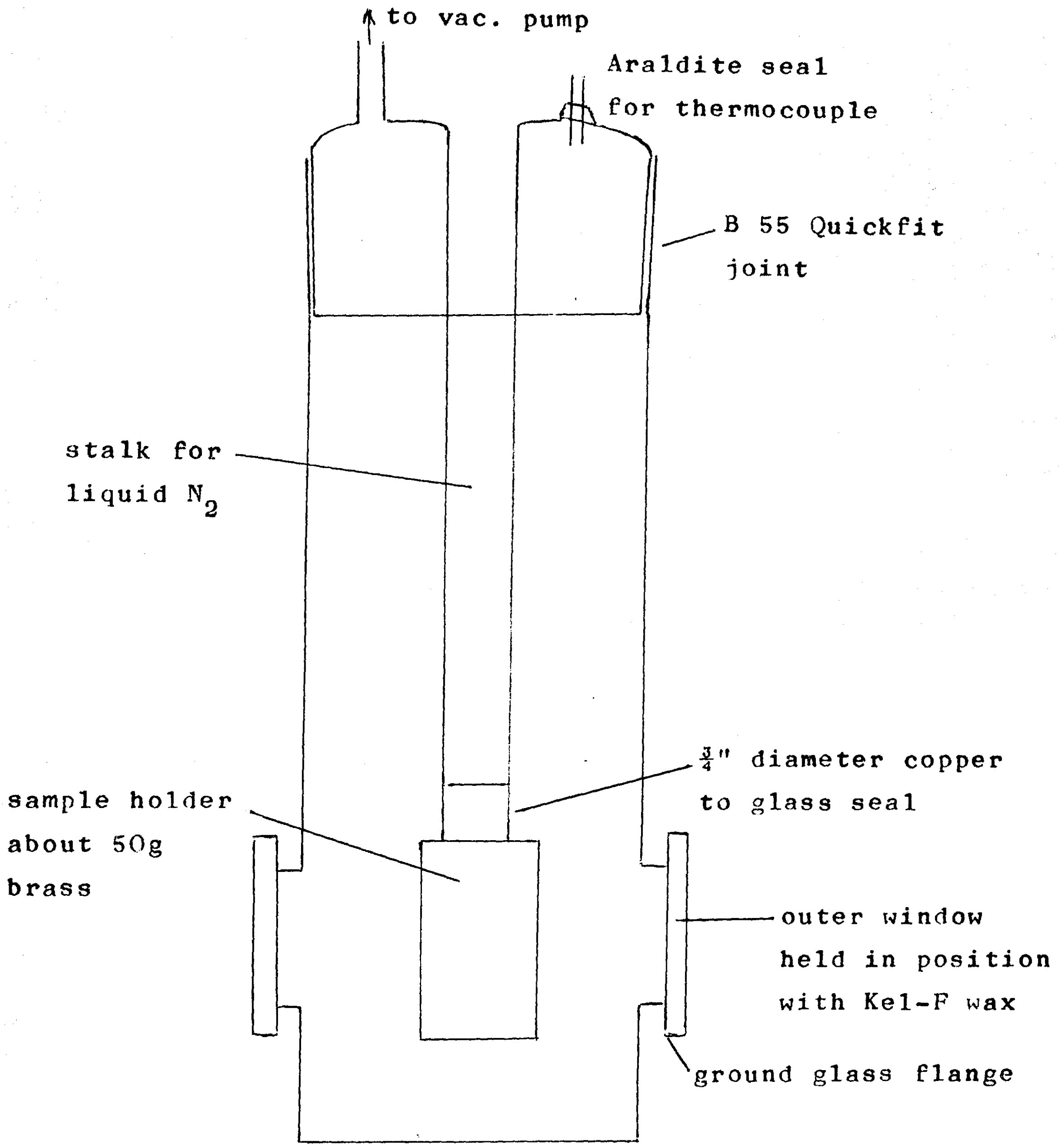


photolysis runs. To try to overcome this problem and to allow inner windows made of hygroscopic materials to be used special cells with glass outer jackets and stalks were constructed (see fig. A-2). These were designed for use with KBr inner windows and so cooled very slowly (>60 min to reach 77K), but could hold a vacuum of 5×10^{-4} torr, while the commercial VLT-2 jackets could be evacuated to $\sim10^{-2}$ torr at best.

Samples were injected into the cells as solutions at room temperature and the cells were then sealed, placed in the jacket which was evacuated, and then cooled so that the solvent formed a glass. The Beckmann FH-01 cells used consist of a stainless steel body encasing lead or teflon gaskets and spacers and two i.r. transmitting windows. A typical arrangement of gaskets and spacer is shown in fig. A-3. Either lead or teflon spacers and gaskets could be used to give a reasonably vacuum tight cell. Teflon was usually used for the front gasket and spacer which come in contact with the sample solution and several lead gaskets were used behind the windows as these distorted on overtightening before any damage to the windows occurred. The nature of the window material will be discussed in section D of this chapter.

Spacers were normally 0.1 mm in thickness, although on occasion 0.25, 0.5, and 1.0 mm spacers were used. A 0.1 mm spacer gave a total cell volume of approximately 0.01 cm^3, but to allow for wastage in cell filling at least 0.05 cm^3 of

Figure A-2: Diagram of glass cell holder and jacket.



I should like to thank Mr. J. Conolly and Mr. J. Nicol for their assistance in the construction of this apparatus.

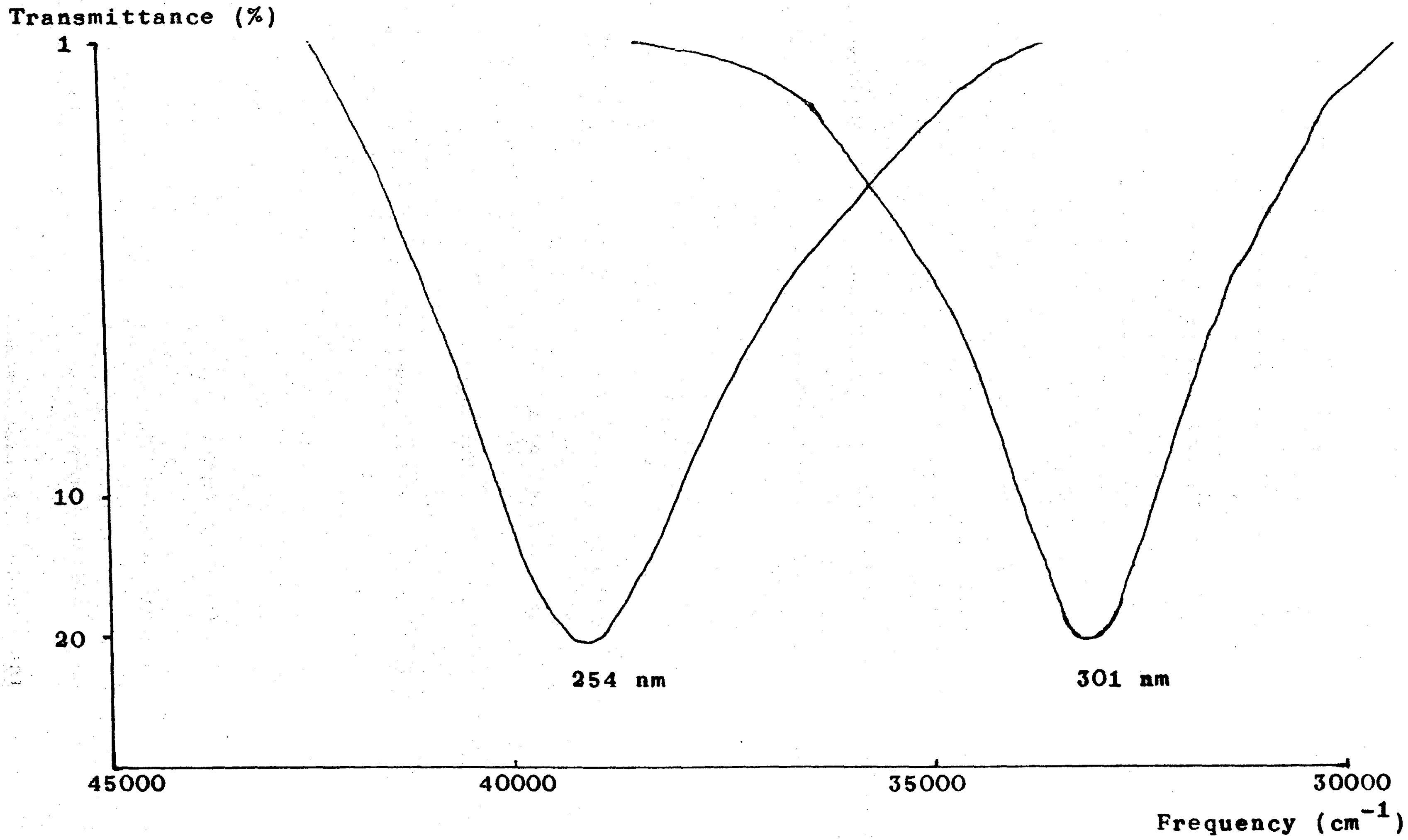
solution had to be used (normally about 0.5 cm^3 was used as the syringe and cell were flushed with sample solution before use). This means that using a 10^{-2}M solution as little as $5x10^{-7}$ moles of starting material are required to carry out a photolysis experiment and the actual amount of material photolysed is less than 10^{-7} moles.

C) Photolysis Conditions

The source of u.v. light in all photolysis experiments was a Hanovia medium pressure mercury discharge lamp which emits 25.18 watts over a wavelength range of 240 to 1367 nm with the main output in the near u.v. (38% of the output betweeen 280 and 370 nm). The amount of light reaching the sample was not reproducible because of absorption and scattering by impurities in the cooling water, principally Fe_2O_3 particles, but the performance of the lamp was monitored regularly by photolysis of standard samples of $Mo(CO)_6$ in 4:1 mch:ip -- complete primary photolysis could normally be achieved in about 35 min using light λ>305 nm. No attempt to measure the intensity of the lamp accurately was made. The quartz parts of the lamp were cleaned as necessary first with dilute nitric acid to remove Fe_2O_3, then with water and Decon 90. Discharge tubes were replaced after about 600h burning. Samples were placed about 10 cm from the lamp in an aluminium box with a shutter between the lamp and sample to allow timed runs to be made.

Figure A-4:

U.V. spectra of Barr and Stroud 'monochromatic' filters used.



Two types of light filters were used: (i) upper energy cut off filters in the form of glass squares (1½ in x 1½ in) were obtained from Chance-Pilkington Ltd. or H.V. Skan Ltd. and characteristics of these filters are shown in fig. A-4 (ii) interference filters transmitting approximately monochromatic light were obtained from H.V. Skan Ltd. or Barr and Stroud Ltd. Characteristics of some of the latter are also shown in fig. A-4. It should be noted that since monochromatic filters transmit only 20-25% of the incident light at their maximum transmission frequency, photolysis using these filters is very slow. In the preceeding chapters filters are referred to only by their trade names (see fig. A-4). In all cases filters in use were fitted to the outer window of the VLT-2 between the lamp and sample. The other outer window was blocked to give reproducible conditions of reflection inside the VLT-2 jacket. The window materials used: calcium fluoride, synthetic sapphire, and potassium bromide all transmit almost 100% of u.v. and visible light.

D) <u>Infrared</u> <u>Spectra</u>

I.r. spectra were normally recorded on Perkin-Elmer 457 or 577 spectrometers, accurate to ±2 cm^{-1} above 2000 cm^{-1} and ±1 cm^{-1} below 2000 cm^{-1}. For specially accurate spectra (±0.5 cm^{-1}) a Perkin-Elmer 225 was used, and for spectra where bands occurred on or very close to 2000 cm^{-1} a PE 257 on Range 1, i.e. with no grating change at 2000 cm^{-1} but a consequent loss of resolution below that frequency, was used. Spectra were calibrated using CO gas or the atmospheric water vapour bands at 1942.6 and 1918 cm^{-1}. The wavenumber marker on the 577 spectrometer was used as calibration on spectra where the x5 scale expansion was employed, but the accuracy of this marker was regularly checked against the 1942.6 and 1918 cm^{-1} water vapour bands.

One of the major problems in this work was the choice of a suitable material for the inner windows of the low temperature cells. The required material must transmit i.r. (preferably over the whole range 4000-250 cm^{-1}), stand repeated cooling to 77K, be reasonably hard to permit the building of leak tight cells and not to distort as the metal of the cell body around it contracts, and transmit u.v./visible light. Table A-1 is a comparison of the relevant properties of commercially available i.r. transmitting materials. None of the materials is ideal. Synthetic sapphire (a form of alumina) was chosen as the best available material, although it had the serious disadvantage of absorbing below 1900 cm^{-1}. Spectra were still obtainable down to about 1700 cm^{-1} (see fig. A-5). Sapphire was found to be almost immune to thermal shock, but would occasionally crack on receiving a mechanical shock. Windows manufactured in different batches were found to vary slightly in thickness and

Figure A-5: Infrared spectrum of sapphire (1 mm path length) in the 2000-1200 cm^{-1} region.

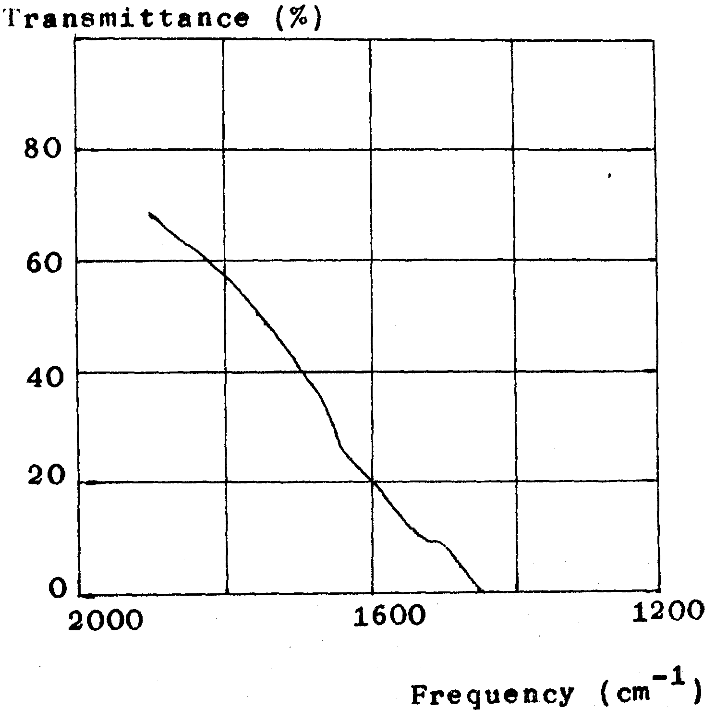


Table A-1: Properties of i.r. window materials.

Material	Useful range (cm^{-1})	Light absorbing (yes/no)	Susceptible to thermal shock?	Rigid?
NaCl	4000-600	no	yes	yes
KBr	4000-400	no	yes	no
CsBr	4000-250	no	no	no
CsI	4000-150	no	no	no
CaF_2	4000-1000	no	yes	yes
AgCl	4000-550	yes	no	no
KRS-5	4000-250	yes	no	no
Sapphire (Al_2O_3)	4000-1800	no	no	yes

Entries in the 'Light absorbing' column refer to absorption of u.v. or visible light, and entries in the 'rigid' column refer to whether the material distorts during use in an FH-01 cell at 77K or not.

this is reflected in some of the spectra where the base line deviates below 1900 cm^{-1} because slightly thicker windows were used in either the sample or reference cell.

Another practical difficulty was cell matching. Although it is easy to match cells at room temperature. the changes which occur on cooling can easily cause mismatch. If any gas bubbles are included in the cell during filling these will not necessarily float to the top as normally happens in solution cells, but may well be included in the glass in the centre of the cell and hence lie in the path of the i.r. beam. This is particularly important where a cell containing a glass containing photolytic fragments and CO is allowed to warm up beyond glass softening temperature and is then refrozen. A mass of tiny bubbles will then often appear in the cell and the actual amount of solution in the i.r. beam will be considerably less than the amount of solvent in the reference cell. Another reason for mismatching of cells on cooling is the difference in degree of contraction between sample and reference cells, but this seems to be of little importance when 0.1 mm spacers and sapphire windows are used. However, in an experiment using KBr windows, the windows distorted so much during cooling that the spacer size had to be increased to 0.25 mm before meaningful spectra could be obtained.

Since synthetic sapphire windows were used only the CO stretching region of the spectrum was normally observed, but even in gas matrix isolation studies[25] where other regions of the spectrum were examined most useful information was obtained from the CO stretching region. As CO stretches are very strongly i.r. active, observation of them alone allowed work with much more dilute solutions than would have otherwise have been possible and so a much better chance of isolation in the glass. It is important to note that the glass forming media themselves absorb in the CO stretching region. Methylcyclohexane has a number of vibrations associated with deformations of the cyclohexane ring which produce a number of weak sharp bands in the 2200-2000 cm^{-1} region, and overtones of C-O stretches in MTHF also produce bands in this region. To overcome this a reference cell containing pure glass at the same temperature as the sample cell was always placed in the reference beam of the spectrometer. This allowed the observation of several weak bands not previously seen by workers using reference cells at room temperature. Although there is bound to be some loss of resolution inherent in this technique of using two cells in sample and reference beams, the spectra obtained are certainly better than those obtained by workers using glass formed by depositing solution on a single, cooled CsBr window and not attenuating the reference beam[54], and the resolution is comparable with some, though by no means all, gas matrix isolation work[55].

A further advantage of sapphire as a window material is its high thermal conductivity relative to alkali halides. This allowed very fast cooling of samples and meant that, although sapphire absorbs most of the i.r. radiation in the spectrometer beam below 1700 cm^{-1}, there was very little heating of the windows while low temperature spectra were being recorded. No temperature increase was recorded by a thermocouple in direct contact with the windows over a period of 10 min in the spectrometer beam with a cell at 77K.

In one experiment a germanium filter about 2 mm in thickness (made by Glasgow University Electrical Engineering Department) was attached to an outer window of the sample cell to remove the visible part of the i.r. spectrometer beam. This filter transmitted about 50% of the i.r. radiation over the range examined and the attenuation of the reference beam required to compensate for its inclusion caused a considerable loss of resolution in the spectra. A similar result was observed in an experiment using a KRS-5 filter.

The previously mentioned tendency for the VLT-2 vacuum jackets to develop leaks which allowed condensation of water on the inner windows was, rather surprisingly, not found to be a serious disadvantage in recording i.r. spectra. Water has no strong absorptions in the 2200-1700 cm^{-1} region and the amount of scattering from a thin water film seems to be minimal.

However, condensation of water on the outer, calcium fluoride, windows had a much greater effect on the i.r. transmission, presumably by causing increased scattering.

E) Ultra-Violet and Visible Spectra

These spectra were recorded using a Pye-Unicam SP 700 spectrometer modified to hold a VLT-2 unit in the sample beam. Air was used as reference throughout. The same cells were used for both i.r. and u.v. spectroscopy as CaF_2 and synthetic sapphire are both transparent in the region examined (165-700 nm). The condensation of water on the inner windows was found to be a much more serious disadvantage in recording u.v spectra and so for detailed u.v. studies it would be advisable to use some purpose built low temperature apparatus rather than a VLT-2. Another practical difficulty was the choice of suitable concentrations. Because of the great difference in extinction coefficients between charge transfer and d--d transitions, two samples of different concentration had to be used to obtain the complete spectrum of each species, and the concentrations required to bring the strongest charge transfer bands on scale at 0.1 mm path length ($\sim 10^{-4}$M) were so low that meaningful i.r. spectra of these solutions or glasses could not be obtained.

Since charge transfer and d--d bands occur in the same region of metal carbonyl spectra and in many cases the spectra of photolysis products were similar to the parent spectra, in many spectra individual bands were impossible to pick out and so very little meaningful information could be obtained from u.v. spectra.

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