MATRIX PHOTOCHEMISTRY OF METAL CARBONYLS

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Abstract. This lecture presents a summary of detailed photochemical studies on metal carbonyls isolated in low-temperature matrices and shows how such studies are of relevance to conventional solution photochemical studies at room-temperature.

INTRODUCTION

Transition metal carbonyls are excellent molecules for photochemical study since most of them are readily soluble in inert solvents, have extremely high UV-vis. extinction coefficients and have high quantum yields for photochemical change. The field has been extensively studied and widely reviewed (1). Two classical examples will illustrate:

\[ \text{Cr(CO)}_6 + \text{P}_3 \xrightarrow{\text{hv}} \text{Cr(CO)}_5 \text{P}_3 + \text{CO}^+ \]

\[ \text{Fe(CO)}_5 \xrightarrow{\text{hv}} \text{Fe}_2(\text{CO})_9^+ \]

An obvious question is, what is the mechanism of such reactions and what intermediates are present? In principle the first reaction can be imagined to proceed by either of two plausible mechanisms:

\[ \text{Cr(CO)}_6 \xrightarrow{-\text{CO}} \text{Cr(CO)}_5 + \text{CO} \]

\[ \text{Cr(CO)}_6 + \text{P}_3 \xrightarrow{\text{hv}} \text{Cr(CO)}_5 \text{P}_3 + \text{CO} \]

Strohmeier's (2) early measurements indicated a quantum yield close to unity, but see later, and, at least at high dilution, that the quantum yield is independent of entering ligand. However, it is important to establish the presence of the pentacordinate intermediate and the obvious way to tackle this is with conventional solution flash photolysis.

Unfortunately this is much more difficult than appears at first sight and contradictory results of flash studies on Cr(CO)_6 in cyclohexane have been published (3). The present position (3b) seems to be that flashing Cr(CO)_6 yields an intermediate with a broad featureless band at \( \lambda_{\text{max}} \approx 503 \text{ nm} \) and with a lifetime, under an atmosphere of CO, of 25 \( \mu \text{s} \). The kinetics of disappearance of the transient are consistent with its being Cr(CO)_5 but no structural information can be obtained from such studies. Flash photolysis studies on Fe(CO)_5 show no transient spectra (within the time resolution of the apparatus available, \( \approx 1 \mu \text{s} \)), but rapid (<10^-4s) formation of Fe_3(CO)_12 (3c). This shows that if Fe(CO)_4 is an intermediate it appears to be much more reactive than Cr(CO)_5.

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There are several problems with such flash studies: minute traces of impurities in the solvent catastrophically interfere with the spectral behaviour; the kinetic interpretation is tricky; the spectral band(s) is (are) very unrevealing. It would be very valuable to obtain infrared spectra of the intermediates in the C-O stretching region since these would provide considerable structural information. There are however severe problems of signal/noise with conventional equipment. Flash photolysis combined with pulsed tunable infrared laser radiation looks very promising and we have such experiments planned using a Spin Flip Raman Laser (4).

Valuable information might be obtained if the fragment were held fixed in an environment where impurity effects are minimised and where spectral information - both vibrational and electronic - is easily obtained. The data could then be used to interpret the solution behaviour. The obvious method is thus the matrix isolation technique (m.i.t.) originally introduced by Lewis but developed by Norman and Porter and more particularly by Pimentel and co-workers (5). Pimentel's version a reactive species is trapped in a large excess of inert rigid matrix - usually a noble gas, N₂, CO - at very low temperatures, and its spectroscopic properties examined at leisure.

The basic assumption of m.i.t. is that the spectroscopic energy levels of the trapped species are only slightly perturbed by the matrix environment. In general this is true, although there are some striking exceptions. The extent of the perturbation of metal carbonyl fragments by the matrix is discussed in detail below.

The species can be trapped in the matrix by several methods: condensation from the gas phase; co-condensation of two reactants; and generation, usually by UV irradiation, from some parent(s) already trapped in the matrix. This lecture is concerned with photochemistry and hence we shall concentrate exclusively on in situ generation - several aspects of photochemistry in matrices have been discussed at length elsewhere (6).

Preliminary encouraging results on Group VI carbonyls were obtained by Orgel and Massey (7) in polymethyl methacrylate at room temperature, and by Sheline and co-workers (8) in hydrocarbon glasses at 77K. Braterman (9) has greatly extended such work. It was our conviction that the use of noble gas matrices at very low temperatures would provide infrared and UV-vis. spectroscopic information that led us some years ago to undertake a detailed investigation of matrix photochemistry of metal carbonyls. These experiments have been gratifyingly productive and in this lecture we describe one particular aspect of this work - the study of fragments of relevance to solution photochemistry, in particular of Cr(CO)₅ and Fe(CO)₄; the mechanism of the matrix photochemical processes; and how this aids interpretation of the solution photochemistry. Experimental details concerning spectrometers, cryogenics etc. are given elsewhere (e.g. ref. 10).

**MATRIX PHOTOCHEMISTRY OF M(CO)₆ (M = Cr, Mo, W)**

1. Generation of 'M(CO)₅ with C₄ᵥ structure

Figure 1 illustrates an experiment on the photochemical behaviour of Cr(CO)₆ in a methane matrix at 20K. Since Cr(CO)₄ is octahedral, the C-O stretching region should contain one infrared active mode of symmetry t₂₂. Figure 1a shows this band at 1985 cm⁻¹; the splitting arises from matrix site effects (10) but for the present purposes it can be ignored. UV photolysis produces striking changes in both infrared and visible spectral regions (figure 1b). The new IR spectrum is consistent with (i) the production of molecular CO whose band position shows it to be still in the matrix cage, (ii) the production of a Cr(CO)₅ fragment of C₄ᵥ symmetry. As expected three CO stretching bands are observed (2A₁ + E). The visible band, labelled 5, grows at the same rate as the IR bands and clearly belongs to the same species.

That the species is indeed the Cr(CO)₅ C₄ᵥ species, and not for example a D₃h Cr(CO)₅ species, is proved by detailed analysis of IR spectra produced on photolysis of randomly substituted Cr(1₃COX(1₂CO)₆₋ₓ) enriched with 50% ¹³CO (11). By using an energy factored force field it was possible to reproduce the observed isotopic spectra with a standard deviation of 0.41 cm⁻¹ on the basis of a C₄ᵥ geometry, and to eliminate a D₃h structure.

This behaviour is consistent with that of earlier workers and is entirely expected. However how does one know that the matrix is not holding the C₄ᵥ fragment in a vice-like grip and that the ideal 'gas-phase' structure of
Cr(CO)$_5$ would not be different? A complete explanation of this requires a careful examination of the rather complex but fascinating matrix photochemistry.

2. Further matrix photochemistry involving Cr(CO)$_5$; matrix perturbation of Cr(CO)$_5$.

An outstanding feature of the photochemical behaviour is shown in Figure 1c. Irradiation into the visible band of the Cr(CO)$_5$ fragment with broad band photolysis or with monochromatic light causes recombination with the CO still in the same matrix cage to give Cr(CO)$_6$. Thus:

\[
\text{Cr(CO)}_5 + \text{CO} \rightleftharpoons \text{Cr(CO)}_6
\]

This experiment is readily repeated with Mo(CO)$_6$ and W(CO)$_6$ and in matrices such as argon, krypton, neon, SF$_6$ etc. However, although the vibrational force field of the pentacarbonyl varies little from matrix to matrix, the position of the visible absorption band is extremely sensitive to matrix varying from 624 nm in Ne to 489 in CH$_4$. Figure 2 represents this data diagrammatically. This enormous variation from Ne to CH$_4$ matrix is unprecedented in matrix studies and the question is whether it arises from a general solvent effect or from a stereospecific interaction involving the Cr(CO)$_5$ empty coordination site. Proof of the latter comes from mixed matrix experiments illustrated in figure 3.
This experiment is reminiscent of mixed-solvent experiments conducted at room-temperature. If the visible shifts in figure 2 were caused by a general solvent effect we should expect a single band in the mixed matrix experiment somewhere between the values for pure Ne and pure Xe. In fact there are two bands corresponding closely to the values in the pure matrices. This demonstrates a stereospecific interaction. Further evidence for this comes from the photochemical behaviour shown in figure 3, where it is clear that a reversible photosubstitution reaction is taking place represented by:

\[
\begin{align*}
\lambda_m &= 628\text{nm} \\
\lambda_m &= 487\text{nm} \\
\lambda \sim 618\text{nm} &\quad \lambda \sim 432\text{nm}
\end{align*}
\]

But what is the origin of this enormous stereospecific shift (4,100 cm\(^{-1} \equiv 12\text{ kcal mol}^{-1} \equiv 50\text{ kJ mol}^{-1})? It seems unlikely that it represents the difference in Ne-Cr and Xe-Cr bond energies in the ground state of the fragments. In fact EHMO calculations (12) suggest that the explanation lies in perturbation of ground and excited states; this is illustrated in figure 4.

The diagram shows: (i) There is interaction between the \(a_1\) orbital (\(d_{z^2}\)) and the filled \(\sigma\) orbital on the matrix species, shown by the dotted line in figure 4. (ii) As the bond angle of the naked fragment is varied the energies of the molecular orbitals, and particularly of the one of \(a_1\) symmetry (\(d_{z^2}\)), change considerably. The \(e/a_1\) energy gap is thus a sensitive function of the angle. The interaction (i), shown below in more detail is the cause of the weak metal-ligand bond, the energy of which is related to \(\delta\). Because of the relative values of the \(d_{z^2}\) orbital energy and the ionization energy of the noble gas, the effect is expected to be greatest for Xe (and CH\(_4\)) and smallest for Ne. This
is confirmed by for instance, an experiment where \( \text{Ar} \ldots \text{Cr(CO)}_5 \) is readily converted to \( \text{CH}_4 \ldots \text{Cr(CO)}_5 \) on warming a \( \text{CH}_4 \)-doped matrix containing \( \text{Ar} \ldots \text{Cr(CO)}_5 \). Thus, at fixed bond angle, and assuming the visible transition is \( b_2^{e} \rightarrow b_2^{e}a_1 \) (see later) the transition is expected to shift to shorter wavelength as the matrix is changed from Ne through to Xe. This is what is observed, but what is the effect of this perturbation on the bond angle?

The intensities of metal carbonyl bands have been much used for structure determination (13) and very detailed analysis (10) of the \( \text{H(CO)}_5 \) IR spectra in the various matrices allows an estimate of the angle \( \theta \) for the fragment in each matrix. The presence of two distinct \( \text{Cr(CO)}_5 \) species in mixed matrices can also be established from the IR spectra. By measuring the relative intensities of the bands of each matrix \( \ldots \text{Cr(CO)}_5 \) species, the bond angles can be compared. Such measurements on \( \text{Cr(CO)}_5 \) in \( \text{Xe}/\text{Ar} \) mixtures show that there is indeed a substantial angle difference between \( \text{Xe} \ldots \text{Cr(CO)}_5 \) and \( \text{Ar} \ldots \text{Cr(CO)}_5 \).
Thus the substitution of Xe for Ar results in a decrease in the angle \( \theta \) and therefore, from figure 4, an increase in the transition energy via this geometry change. The two effects (i) and (ii) above then act in concert in shifting the visible transition to shorter wavelength in the series Ne, Ar, Xe, CH\(_4\). It is difficult to estimate however the relative importance of each effect.

The interactions of Cr(CO)\(_5\) with Xe and CH\(_4\) are not perhaps so surprising when it is remembered that Xe...Cr(CO)\(_5\) is isoelectronic with the well known species [ICr(CO)\(_5\)] and that Cotton and Day (14) recently reported the crystal structure of \((\text{C}_2\text{H}_5)\_2\text{B}(\text{pyrazolyl})(\text{C}_7\text{H}_7)\text{Mo(CO)}\(_2\) in which, even at room temperature, there is a definite interaction between the Mo atom and one of the \(\alpha\) C-H bonds of the ethyl groups; the hydrogen atom actually occupies the sixth coordination site around the molybdenum atom, in what would otherwise be a 16-electron compound.

The Ne....Cr(CO)\(_5\)/Xe....Cr(CO)\(_5\) exchange argues for considerable mobility (where for the moment we make no assumption about the nature of the mobility in the matrix) and it seems very unlikely that the ground state Cr-Ne interaction could be strong enough to force the fragment to adopt the C\(_{2v}\) geometry rather than some other. Thus this argues for a 'gas-phase' C\(_{2v}\) structure, but more of this shortly.

Since Cr(CO)\(_5\) interacts weakly with noble gases via the empty coordination site it is not surprising to find that with more 'conventional' ligands, well characterised compounds can be synthesised. Rest (15) first demonstrated that photolysis of Ni(CO)\(_4\) in N\(_2\) leads to Ni(CO)\(_3\)N\(_2\) with IR frequencies close to those later obtained by Ozin (16) on co-condensation of Ni(CO)/N\(_2\). Photolysis of e.g. Mo(CO)\(_6\) in a matrix of pure N\(_2\) causes generation of N\(_2\)Mo(CO)\(_5\) (17); photolysis in a mixed matrix of N\(_2)/Ar\) causes generation of N\(_2\)Mo(CO)\(_5\) and Ar....Mo(CO)\(_5\) - where, perhaps arbitrarily, we represent a weak interaction with a dotted line and a strong interaction with no spacing. These two species have very different absorption bands and can be readily interconverted in the Ne....Cr(CO)\(_5\)/Xe....Cr(CO)\(_5\) manner:

\[
\begin{align*}
\text{N}_2\text{Mo(CO)}\(_5\) & \rightarrow \text{367 nm} \quad \text{Ar}....\text{Mo(CO)}\(_5\) \\
\text{367 nm} & \rightarrow 432 \text{ nm} \quad \text{Ar}....\text{Mo(CO)}\(_5\)
\end{align*}
\]

To return to matrix mobility. Conclusive evidence for mobility of the carbonyl intermediates comes from experiments on the matrix....M(CO)\(_5\) and N\(_2\)M(CO)\(_5\) species using plane polarised light for both photolysis and IR/UV-vis. spectroscopy.

3. Photochemistry and spectroscopy with polarized light.

**Introduction.** If an individual molecule (A) with a single optic axis is held absolutely rigid in a matrix then the probability of absorption of plane polarized light falling by the sample is as illustrated in figure 5. If the absorption of light leads to production of a new chemical species (B), with its optic axis in the same direction as the reactant (A), then if there is no orientational change at any stage of the photochemical act, the contribution to the polarized absorption spectra of B by the single molecule is given by \( \text{Ivert (contribution } \alpha \cos^2 \theta) \), \( \text{Ihorz (contribution } \alpha \cos^4 \theta) \). Suppose there is a random orientation of A molecules at the beginning, the nearer \( \theta \) is to 90° for a particular molecule, the less likely is that molecule to absorb and hence to be photolysed; thus, as photolysis proceeds, the spectrum of the remaining sample of A shows developing dichroism because of non-random selection of molecules for photolysis - 'dichroic photodepletion'. Meanwhile, the spectrum of B develops with the opposite dichroism - 'dichroic photoproduction'. If the matrix allows some degree of rotational diffusion then study of the spectrum of B by either polarized fluorescence (for fast rotation) or polarized absorption spectroscopy (for slow rotation) gives information about rotation rates and viscosity (18). More interesting in the present context are experiments where the matrix allows no rotational diffusion of A or B, i.e. in the absence of further photolysis the dichroism of A and B can be maintained indefinitely at low temperature. However, if A shows developing dichroic photodepletion and B shows little or even no dichroic photoproduction, then we can conclude that some intermediate is mobile during the photochemical act. We have observed several examples of this in low-temperature matrices and have used polarized IR/UV-vis. spectroscopy to assign bands and to provide valuable information about photochemical intermediates (19). In the present context of metal carbonyls two examples will illustrate.
Matrix photochemistry of metal carbonyls

Fig. 5
Absorption probabilities of molecules

Polarized matrix photochemistry of matrix..., M(CO)_5 and N_2M(CO)_5. In the mixed N_2/Ar matrix we have:

\[
\text{N}_2\text{Mo(CO)}_5 \xrightarrow{\text{hv pol}} \text{Ar}...\text{Mo(CO)}_5
\]

(R = random; O = oriented; pol. = polarized; measurements using polarized visible spectra.)

Thus photolysis of randomly oriented dinitrogen complex produces oriented N_2 complex by dichroic photodepletion but there is no orientation in the product, Ar...Mo(CO)_5. Moreover reversal of the reaction:

\[
\text{Ar}...\text{Mo(CO)}_5 \xrightarrow{\text{hv pol}} \text{N}_2\text{Mo(CO)}_5
\]

shows developing orientation of the pentacarbonyl and no developing orientation of the N_2 complex. Thus both species can be held oriented in the matrix, but this can only be achieved by photodepletion - during photolysis something happens to randomize the product.

This is even more strikingly demonstrated by our experiments on 'photoreorientation', an effect first observed by Teitel (20), discussed by Albrecht (21), and exploited by Stolbova and co-workers (22) in studies of organic dyes in 77K glasses. We have investigated the photoreorientation of several molecules in matrices but we concentrate here on CH_4...Cr(CO)_5, which illustrates the technique and provides photochemical information.

It is instructive to first note how the A_1 and E C-O stretching modes of differently oriented pentacarbonyl molecules are expected to interact with differently polarized IR light - figure 6 considers just the three extreme orientations. Preferred orientation is clearly readily detectable by polarized IR spectra.

Figure 7 illustrates a polarized experiment with CH_4...Cr(CO)_5. On UV generation of CH_4...Cr(CO)_5 from Cr(CO)_6 the 'vert' and 'horiz' spectra have the same intensity (not illustrated). On visible (λ>375 nm) polarized irradiation dichroism develops in both IR and vis. bands; rotating the polarization of the irradiating beam by 90° reverses the spectral dichroism; which can be returned to the original value on turning the polarizing radiation back again. The obvious first interpretation is that the dichroism results from developing dichroic photodepletion according to:

\[
\text{CH}_4...\text{Cr(CO)}_5 + \text{CO} \xrightarrow{\text{hv pol}} \text{Cr(CO)}_6
\]

(necessarily isotropic)
However the net gain in the intensity of the visible band with vertical polarization on going from a) → b) cannot be accounted for by simple photodepletion.

Thus the Cr(CO)$_5$ fragment must be reoriented or 'turned over' as a result of absorption of the visible radiation. Since the visible absorption band (figure 7) behaves in the opposite sense to the carbonyl $a_1$ IR band and in the same sense as the $e$ mode (not shown) one can positively assign this visible band to a transition of species E (q.v.). Thus the photoreorientation can be schematically represented for two orientations:
We do not of course know how far each molecule rotates on absorption of a photon. The diagram simply illustrates that, as the photolysis proceeds, \( X \rightarrow Y \) after perhaps several photon absorptions. Once a molecule is in orientation \( Y \) it is 'blind' to polarizing \( \text{horiz} \) radiation. Reversing the orientation of polarized photolysis will build up the concentration of \( X \). In theory photolysis should proceed until all molecules are in orientation \( Y \) (or \( X \)) and the dichroic ratio is infinite. In practice, for reasons discussed elsewhere (23) this is never achieved but ratios of \( \text{vert} / \text{horiz} \) as high as 2 are readily obtained.

We can see that the matrix holds the fragment rigid at the beginning and the end - i.e. when cold - but there is mobility during the photochemical act. How precisely does this reorientation occur?

4. 'M(CO)\( _5 \)' matrix photochemistry - the detailed pathway.
There is very strong evidence (1) from solution photochemistry that species such as \( \text{Ar}...\text{Cr(CO)}\( _5 \) or \( \text{N}_2\text{Cr(CO)}\( _5 \) are expected to eject the 'ligand' on absorption of visible radiation. Thus it is 'naked' \( \text{Cr(CO)}\( _5 \) that is being reoriented in the matrix. There are two obvious mechanisms for this reorientation, a simple rotation or a specific intramolecular rearrangement. That the latter is more likely is shown by experiments on thio carbonyl (CS) species where the CS group acts in many ways like a labelled CO group. In particular, \( \text{Ar}...\text{Cr(CO)}\( _4\text{CS} \) generated by UV photolysis of \( \text{Cr(CO)}\( _5\text{CS} \) shows wavelength dependent isomerism (24).

\[
\begin{align*}
\lambda_m = 525\text{nm} & \quad \lambda_m = 562\text{nm} \\
\text{CS} & \\
\text{Ar} \quad \lambda \sim 489\text{nm} & \quad \lambda \sim 618\text{nm} \\
\text{CS} & \\
\text{Ar}
\end{align*}
\]

The most probable pathway for this rearrangement and for the reorientation of \( \text{Cr(CO)}\( _5 \) is via a trigonal bipyramidal intermediate configuration. EHMO calculations (25) underscore this interpretation and the mechanism can be schematically represented for the naked \( \text{Cr(CO)}\( _5 \) as in figure 8.

Irradiation of matrix...\( \text{Cr(CO)}\( _5 \) with visible light results in ejection of the matrix species and formation of naked \( \text{Cr(CO)}\( _5 \) in the excited state 'E - a process discussed in more detail elsewhere (23). This state is identical to a highly vibrationally excited state of the \( D_{3h} \) configuration. The \( C_4\text{V} \) configuration relaxes to the \( D_{3h} \) structure which returns to the \( C_4\text{V} \) (\( 'A_1' \)) ground state with the same or a different orientation from the original matrix...\( \text{Cr(CO)}\( _5 \) molecule. The overall mechanism is the square pyramidal analogue of the Berry process. We can represent the interchange by a correlation diagram:
These results have two significant consequences:

a) The reorientation makes it extremely unlikely that the structures adopted by matrix isolated carbonyls are determined by a 'clamping' effect. The fact that the orientation mechanism probably involves $D_{3h}$ structure argues that if this were the most stable configuration, the molecule would have ample opportunity of adopting this structure. (It is worth noting that there is no way that structures of the intermediate can be proved from studies on the reactants and products.)

b) We can now explain all the matrix photochemistry of $M(\text{CO})_5$, including the reversal to $M(\text{CO})_6$ described at the beginning. This is shown in figure 9.
UV photolysis of Cr(CO)$_6$ in say Ar/N$_2$ gives CO and excited, naked Cr(CO)$_5$ which rearranges via the D$_{3h}$ configuration to ground state C$_{4v}$ with several possible orientations - figure 9 shows three possibilities. If the final orientation of Cr(CO)$_5$ is the same as in the initially excited state of photoproduced Cr(CO)$_5$ the fragment will simply recombine with CO to reform Cr(CO)$_6$. If the empty coordination site points at Ar, Ar... Cr(CO)$_5$ is formed; if at N$_2$, N$_2$Cr(CO)$_5$ is formed. Thus the mechanism explains the long-standing problem of the escape of the photoejected CO from the vacant site of the fragment. That rearrangement occurs in the excited Cr(CO)$_5$ from Cr(CO)$_6$ is supported by an experiment on $^{13}$CO labelled W(CO)$_5$CS (24), where it can be shown that the five-coordinate species undergoes an excited state rearrangement after ejection of CO from the parent molecule.

Irradiation into the visible band of Ar... Cr(CO)$_5$ gives excited C$_{4v}$ Cr(CO)$_5$, then D$_{3h}$ Cr(CO)$_5$ and then ground state C$_{4v}$ Cr(CO)$_5$ with again several possible orientations. If the empty site faces CO we have regenerated Cr(CO)$_6$. If the
empty site faces an argon atom Ar....Cr(CO)₅ is reformed, and can be photolysed again. If it faces an N₂ molecule we form N₂Cr(CO)₅ which does not absorb at the frequency used and there is therefore overall conversion of Ar....Cr(CO)₅ to N₂Cr(CO)₅. Interconversion among the matrix isolated species is thus facile, due to the ability of the naked fragment to 'scan' the whole solid angle of its environment. We have thus pinned down the orientational behaviour to an intramolecular rearrangement process and suggested a probable candidate.

This mechanism, which fits all the photochemical results so far considered, also explains several other features of the matrix behaviour of carbonyls which we shall return to shortly; but now consider the application of this complex matrix photochemistry to room temperature solution carbonyl photochemistry.

**SOLUTION PHOTOCHEMISTRY OF M(CO)₆ AND Fe(CO)₅**

**Cr(CO)₆ in cyclohexane**

Extrapolating the matrix photochemistry to the room-temperature solution photochemistry of dilute Cr(CO)₆ in cyclohexane the following predictions can be made.

a) The primary photochemical act will be ejection of CO from Cr(CO)₆ to give naked excited Cr(CO)₅ with the C₄ᵥ structure; this will very rapidly rearrange via the D₃h configuration to the C₁ᵥ ground state structure. Because of the 'cage effect' there will be a finite probability of the Cr(CO)₅ re-encountering the ejected CO before either have escaped from the solvent cage. The quantum yield for photochemical change should therefore be less than unity. In very recent experiments Nasielski (27) has re-examined the quantum yield experiments for photosubstitution and concludes that the value is, not unity, but 0.67. If the C₄ᵥ → D₃h → C₁ᵥ pathway were followed exactly in solution, the probability of reorientation towards the photoejected CO would be 1/3 and hence the maximum photosubstitution quantum yield would be 2/3, very close to the value obtained by Nasielski.

b) The majority of the naked Cr(CO)₅ molecules will orient with the coordination site opposite cyclohexane solvent molecules. By analogy with CH₄....Cr(CO)₅ at 20K, a weak cyclohexane (solv)....Cr(CO)₅ complex is expected. At room temperature an equilibrium will exist between naked and weakly complexed Cr(CO)₅.

\[
\text{K} = \frac{[\text{solv}....\text{Cr(CO)₅}]}{[\text{solv}][\text{Cr(CO)₅(n)}]} \quad (n \equiv \text{naked})
\]

Although the equilibrium constant is not expected to be very different from unity, the very large excess of cyclohexane (cyclohexane: carbonyl =105:1) will mean that most Cr(CO)₅ molecules are in fact weakly bonded to the solvent. Thus the species detected by flash photolysis is actually solv....Cr(CO)₅. This is confirmed by the observation that λ_max in cyclohexane is 503 nm - not far from the hydrocarbon glass matrices (493 nm) and CH₄ matrix (489 nm) and a very long way from what is presumably the nearest practical approach to naked Cr(CO)₅ in the matrix, Ne....Cr(CO)₅ at 624 nm.

\[
\text{Rate} = k[Cr(CO)₅(n)][CO] \quad \text{(rate of recombination with CO)}
\]

assumed, as seems reasonable, that the reaction proceeds via an SN₁ mechanism. Since [Cr(CO)₅(n)] is low, the rate is relatively slow (cf. Fe(CO)₄ later).

\[
\text{Rate} = k \frac{[\text{solv}....\text{Cr(CO)₅}][CO]}{K [\text{solv}]}
\]

From the matrix data we know that the interaction of Cr(CO)₅ with CH₄ or hydrocarbon/glass is greater than with CF₄. We predict therefore that in solution, the interaction of Cr(CO)₅ with cyclohexane will be greater than with saturated fluorocarbon. Hence in the rate equation, K for cyclo....Cr(CO)₅ > (F)....Cr(CO)₅ and we predict that the recombination rate of 'Cr(CO)₅' with CO will be faster in fluorocarbon than hydrocarbon. Kelly (28) has measured these rates:

<table>
<thead>
<tr>
<th>solvent</th>
<th>cyclohexane</th>
<th>C₇F₁₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1\text{ mol}^{-1} \text{ s}^{-1})</td>
<td>(3 \times 10^6)</td>
<td>(3.5 \times 10^8)</td>
</tr>
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These values are in remarkable agreement with the predictions. An analogous argument can be developed if it is assumed that the reaction of solv. Cr(CO)₅ with CO proceeds via a seven-coordinate intermediate. We turn now to the solution photochemistry of the second example from the Introduction, Fe(CO)₅.

**Fe(CO)₅ in cyclohexane**

First we consider what can be learned from a study of this species in low-temperature matrices. We have examined extensively the photochemistry of this molecule (29) by the same techniques as for Cr(CO)₆. For the purpose of this lecture two results are of significance.

\[ \text{hv(UV)} \quad \text{Fe(CO)₅} \quad \text{hv(nir,vis)} \quad \text{Fe(CO)₄} + \text{CO} \]

In the argon matrix (also Ne) there is no evidence for any stereospecific argon/Fe(CO)₄ interaction. With CH₄ (also xenon), two spectroscopically and structurally distinct forms of Fe(CO)₄ can be produced and interconverted as shown. One of these species is uncomplexed and is essentially the same fragment as in argon; the other forms a stereospecific CH₄ complex. It is important to note the contrast with Cr(CO)₅ in matrices, where it has not been possible to observe the naked fragment under any conditions.

\[ \text{hv(UV)} \quad \text{Fe(CO)₅} \quad \lambda>320\text{nm} \quad \text{Fe(CO)₄} \quad \lambda>320\text{nm} \quad \lambda>375\text{nm} \quad \text{CH₄Fe(CO)₄} \]

All distorted tetrahedral d⁸ complexes are paramagnetic (triplet) and all flat (square planar) d⁸ complexes are diamagnetic (singlet). Molecular orbital calculations suggest that naked triplet Fe(CO)₄ has a C₂ᵥ structure with bond angles ~135°, ~110° close to those observed ~140°, ~120° and that the five-coordinate CH₄Fe(CO)₄ is in a singlet state. However, as yet we have no experimental evidence for the spin states.

Since naked Fe(CO)₄ can exist when surrounded by a matrix of methane, it is not unreasonable to suppose that in cyclohexane it is also capable of independent existence. We can now be very speculative and suggest the following scheme.

\[ \text{Fe(CO)₅} \quad \text{hv flash} \quad \text{Fe(CO)₄ (naked, triplet)} \quad \text{slow solv...Fe(CO)₄ (singlet)} \]

During the flash Fe(CO)₅ is converted to Fe(CO)₄; this reacts very rapidly with itself through Fe₂(CO)₈ to Fe₃(CO)₁₂. In this scheme naked Fe(CO)₄ reacts with itself so much faster than with the solvent that no solv...Fe(CO)₄ is detected within the time resolution of the conventional flash photolysis equipment. Thus the reason that Fe(CO)₄ appears to be more reactive than Cr(CO)₅ in flash photolysis experiments may be that naked Fe(CO)₄ is in fact less reactive towards the solvent than naked Cr(CO)₅.
FURTHER MECHANISTIC POINTS

We wish to conclude this lecture by drawing together a few more points concerned with metal carbonyls in matrices which are readily explained using the picture of the matrix environment now established.

Cr(CO)$_5$ in a pure CO and in CO/Ar mixed matrices

It is at first sight very surprising that monochromatic photolysis of Cr(CO)$_6$ in a pure CO matrix gives Cr(CO)$_5$ (31). Similarly Fe(CO)$_5$ can be generated in a CO matrix from Fe(CO)$_5$ (29). The visible band of the Cr(CO)$_5$ fragment is at 462 nm, implying a stronger interaction of Cr(CO)$_5$ with the matrix CO, than with CH$_4$. The interaction cannot be directly OC-...Cr since this would simply be Cr(CO)$_6$; presumably the species is bonded either through the oxygen or side-ways: CO-...Cr(CO)$_5$ or O-...Cr(CO)$_5$, but we have not been able to assign an IR band to the interacting CO. This species can also be generated, in the presence of large excess of Cr(CO)$_6$, by cocondensation of Cr atoms with CO (31) - a technique also beautifully exploited by Ogden (32), Ozin (33) and others.

It is no surprise that the reverse reaction, CO-...Cr(CO)$_5$ to Cr(CO)$_6$ is readily promoted by irradiation at ~460 nm. However, warming the matrix even to near the boil-off temperature, shows no thermal reversal - presumably the interaction is sufficiently strong to prevent this reversal.

In a mixed CO/Ar matrix, both CO-...Cr(CO)$_5$ and Ar-...Cr(CO)$_5$ can be generated. Interestingly in matrices with excess CO, Ar-...Cr(CO)$_5$ does thermally reverse to Cr(CO)$_6$ on warming the matrix but CO-...Cr(CO)$_5$ does not. The different behaviour with Ar and CO as 'ligand' is gratifyingly in line with the conclusions from visible data about relative strengths of interaction.

Ni(CO)$_3$ in matrices

It is extremely difficult to generate Ni(CO)$_3$ by photolysis of Ni(CO)$_4$ in, say, argon (34). Once generated it cannot be photochemically reconverted to Ni(CO)$_4$ but slight warming very quickly promotes recombination. These observations are probably a reflection of the fact that Ni(CO)$_4$ and Ni(CO)$_3$ absorb in the same part of the spectrum (35), that Ni(CO)$_3$ is only observed when CO is ejected out of matrix cage, and that it is very difficult to envisage how the D$_3h$ Ni(CO)$_3$ fragment could 'turn its back' on the photoejected CO.

Efficiency of photoreorientation

Finally there is the interesting observation that the efficiency of photolysis and photoreorientation is a function of matrix. Photochemical production of highly unsaturated carbonyl fragments e.g. Mo(CO)$_4$ or Fe(CO)$_3$ is much more efficient in CH$_4$ than Ar matrices. Similarly, Cr(CO)$_5$ is more easily photoreoriented in CH$_4$ than in Ar matrices. These differences have been put on a quantitative basis by measurement (36) of the ratio of quantum yields for the production of Mo(CO)$_5$ by UV light and its destruction by visible light,

\[ \frac{\phi_{\text{vis}}}{\phi_{\text{UV}}} \]

<table>
<thead>
<tr>
<th>CH$_4$</th>
<th>Ar</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.04</td>
<td>0.2</td>
<td>6</td>
</tr>
</tbody>
</table>

These results may be due to a smaller degree of mobility of M(CO)$_5$ in CH$_4$ than in the rare gas matrices, consistent with a more rapid 'freezing out' of the excited M(CO)$_5$ fragment in the molecular matrix. Thus the different quantum yields may reflect the efficiency of energy transfer from the excited, trapped molecule to the matrix medium.

This lecture has shown how matrix isolation has not only allowed us to characterize Cr(CO)$_5$ and Fe(CO)$_4$ in considerable detail but has also produced several interesting ideas which appear to be of importance in the solution photochemistry of these species. It is clear that although not all aspects of the photolysis mechanism are fully understood yet, the transition metal carbonyls provide an ideal means of probing photochemical and photophysical processes.
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