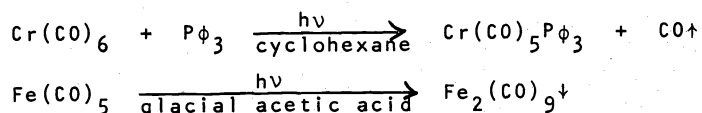MATRIX PHOTOCHEMISTRY OF METAL CARBONYLS[*]

J.J. Turner[†], J.K. Burdett, R.N. Perutz and M. Poliakoff

Department of Inorganic Chemistry, The University, Newcastle-upon-Tyne, NE1 7RU, England

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:

$$Cr(CO)_6 + P\phi_3 \xrightarrow[\text{cyclohexane}]{h\nu} Cr(CO)_5 P\phi_3 + CO\uparrow$$

$$Fe(CO)_5 \xrightarrow[\text{glacial acetic acid}]{h\nu} Fe_2(CO)_9\downarrow$$

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:
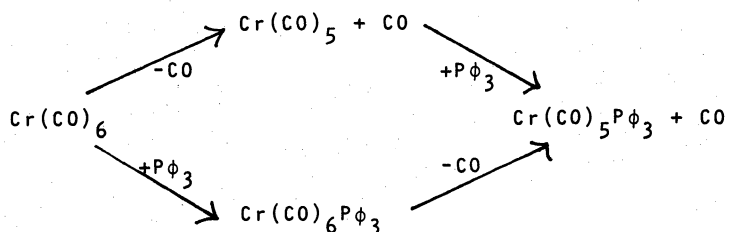
Strohmeier's (2) early measurements indicated a quantum yield close to unity, but see later, and, at least at high dilution, that the quantum yield is independent of entering ligand. However, it is important to establish the presence of the pentacoordinate intermediate and the obvious way to tackle this 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 λ_{max} ~503 nm and with a lifetime, under an atmosphere of CO, of 25 μs. 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, ~1 μs), but rapid ($<10^{-4}$s) 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 $Cr(CO)_5$.

There are several problems with such flash studies: minute traces of im-
purities 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 <u>infrared</u> spectra of the
intermediates in the C-O stretching region since these would provide con-
siderable 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 exper-
iments 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 inform-
ation - <u>both</u> vibrational and electronic - is easily obtained. The data could
then be <u>used</u> 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). In Pimentel's version a reactive species is trapped in a large excess
of inert rigid matrix - usually a noble gas, N_2, 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 <u>photochemistry</u> and hence we shall concentrate exclus-
ively 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, combined with both infrared and UV-vis. spectroscopy,
would lead to detailed photochemical and structural 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 con-
cerning spectrometers, cryogenics etc. are given elsewhere (e.g. ref. 10).

MATRIX PHOTOCHEMISTRY OF $M(CO)_6$ (M = Cr, Mo, W)

<u>1. Generation of '$M(CO)_5$' with C_{4v} structure</u>
Figure 1 illustrates an experiment on the photochemical behaviour of $Cr(CO)_6$ in
a methane matrix at 20K. Since $Cr(CO)_6$ is octahedral, the C-O stretching reg-
ion should contain one infrared active mode of symmetry t_{1u}. 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 C_{4v} symmetry. As expected three CO stretching bands are
observed ($2A_1$ + 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 $Cr(CO)_5$ C_{4v} species, and not for example a D_{3h}
$Cr(CO)_5$ species, is proved by detailed analysis of IR spectra produced on
photolysis of randomly substituted $Cr(^{13}CO)_x(^{12}CO)_{6-x}$, enriched with ~50% ^{13}CO
(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 C_{4v} geometry, and to eliminate a D_{3h} 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 C_{4v}
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.
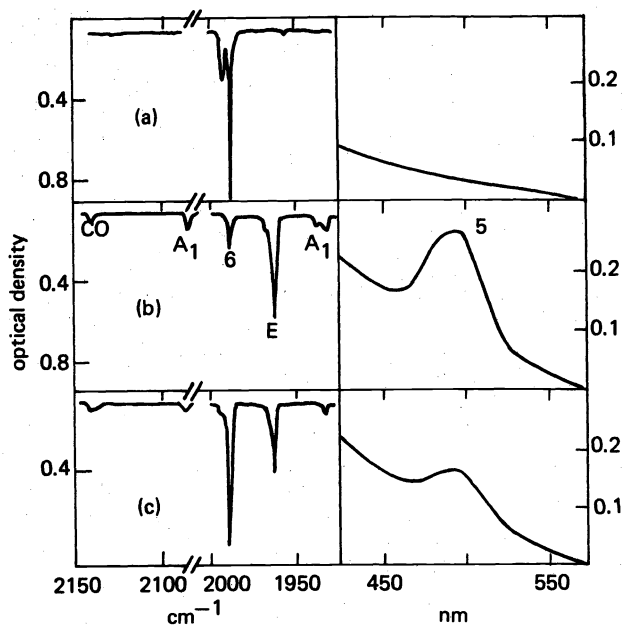

Fig. 1
IR and UV-vis spectra of $Cr(CO)_6$ in a CH_4 matrix at 20K.
(a) after sample deposition
(b) after 30 sec photolysis with unfiltered medium pressure mercury lamp (5 & 6 = bands due to $Cr(CO)_5$ and $Cr(CO)_6$)
(c) after 1.5 min photolysis with $\lambda > 330nm$.

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:

ir	$1985cm^{-1}$	$2088,1961,1932cm^{-1}$
UV,vis	227,280nm	~230,489nm (in CH_4 matrix)
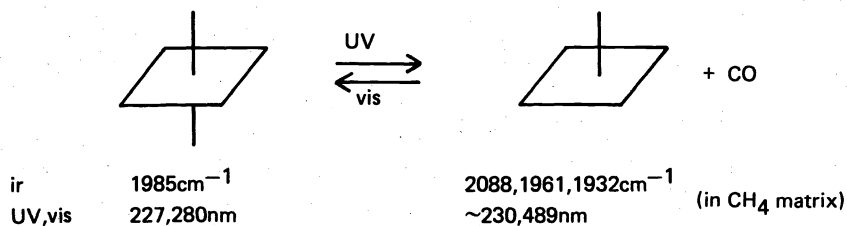
This experiment is readily repeated with $Mo(CO)_6$ and $W(CO)_6$ and in matrices such as argon, krypton, neon, SF_6 etc. However, although the vibrational force field of the pentacarbonyl varies little from matrix to matrix, the position of the visible absorption band is extremely sensitive to matrix 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.

Fig. 2
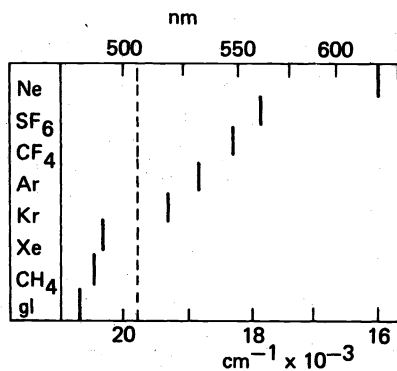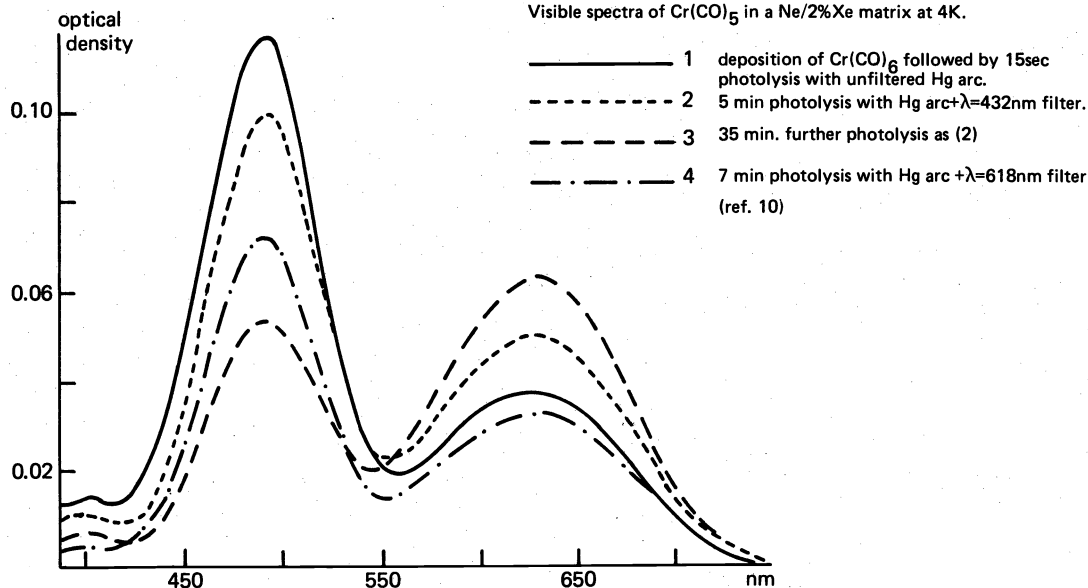Diagrammatic representation of the visible band of $Cr(CO)_5$ in different matrices (plot is linear in cm^{-1}).
gl = glass,
broken line = value from flash photolysis of $Cr(CO)_6$ in cyclohexane sol. (ref.3b).
Matrix data from ref.10.

Fig. 3
Visible spectra of $Cr(CO)_5$ in a Ne/2%Xe matrix at 4K.

————————— 1   deposition of $Cr(CO)_6$ followed by 15sec photolysis with unfiltered Hg arc.

– – – – – – – 2   5 min photolysis with Hg arc+λ=432nm filter.

— — — — — 3   35 min. further photolysis as (2)

— · — · — 4   7 min photolysis with Hg arc +λ=618nm filter

(ref. 10)

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 photo-chemical behaviour shown in figure 3, where it is clear that a reversible photosubstitution reaction is taking place represented by:
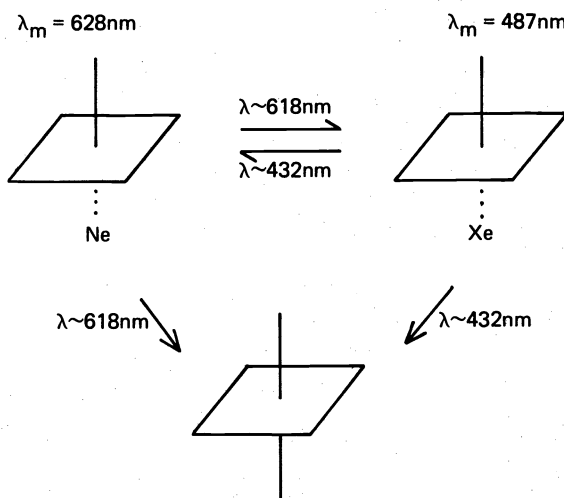
But what is the origin of this enormous stereospecific shift ($4,100$ cm^{-1} ≡ 12 kcal mol^{-1} ≡ 50 kJ mol^{-1}). It seems unlikely that it represents the diff-erence in Ne-Cr and Xe-Cr bond energies in the ground state of the fragments. In fact EHMO calculations (12) suggest that the explanation lies in perturb-ation of ground and excited states; this is illustrated in figure 4.

The diagram shows: (i) There is interaction between the a_1 orbital (d_z2) and the filled σ orbital on the matrix species, shown by the dotted line of 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_z2), 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 δ. Because of the relative values of the d_z2 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

$$d_{x^2-y^2}$$ _____ — — — — _____

$$d_{z^2}$$ _____ — — — _____

$$d_{xz}, d_{yz}$$
$$d_{xy}$$ ligand σ

δ
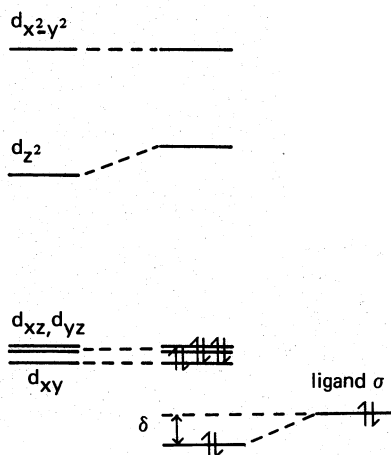
is confirmed by for instance, an experiment where Ar....Cr(CO)$_5$ is readily con-
verted to CH$_4$....Cr(CO)$_5$ on warming a CH$_4$-doped matrix containing Ar...Cr(CO)$_5$.
Thus, at fixed bond angle, and assuming the visible transition is $b_2{}^2e^4 \rightarrow$
$b_2{}^2e^3a_1{}^1$ (see later) the transition is expected to shift to shorter wavelength
as the matrix is changed from Ne through to Xe. This is what is observed, but
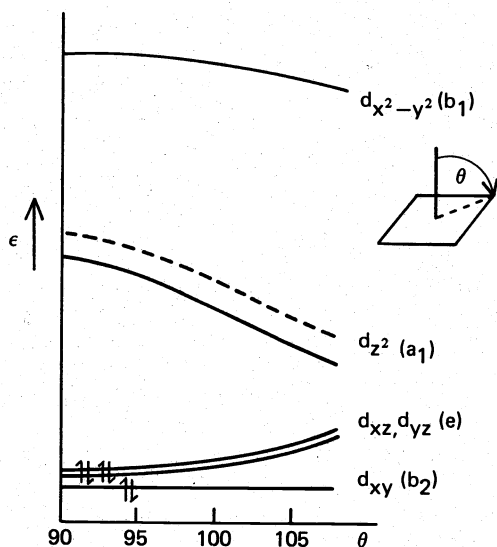what is the effect of this perturbation on the bond angle?

ϵ

$$d_{x^2-y^2} (b_1)$$

θ

$$d_{z^2} (a_1)$$

$$d_{xz}, d_{yz} (e)$$

$$d_{xy} (b_2)$$

90   95   100   105 θ

Fig. 4
Molecular orbital energy diagram
as a function of axial-equatorial
angle θ for an M(CO)$_5$ fragment
showing destabilisation of the
d_{z^2} orbital due to interaction
with a ligand σ orbital.

The intensities of metal carbonyl bands have been much used for structure
determination (13) and very detailed analysis (10) of the M(CO)$_5$ IR spectra in
the various matrices allows an estimate of the angle θ for the fragment in each
matrix. The presence of two distinct Cr(CO)$_5$ species in mixed matrices can
also be established from the IR spectra. By measuring the relative intensit-
ies of the bands of each matrix ....Cr(CO)$_5$ species, the bond angles can be
compared. Such measurements on Cr(CO)$_5$ in Xe/Ar mixtures show that there is
indeed a substantial angle difference between Xe....Cr(CO)$_5$ and Ar....Cr(CO)$_5$.

θ θ

Xe   Ar

θ(from ir) 91.3°   95.5°
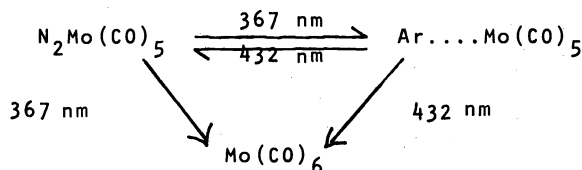
λ_m(vis)   492nm   533nm
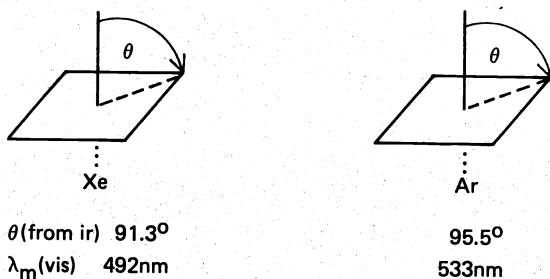
Thus the substitution of Xe for Ar results in a decrease in the angle θ and
therefore, from figure 4, an increase in the transition energy via this geometry
change. The two effects (i) and (ii) above then act in concert in shifting
the visible transition to shorter wavelength in the series Ne, Ar, Xe, CH₄.
It is difficult to estimate however the relative importance of each effect.

The interactions of $Cr(CO)_5$ with Xe and CH₄ 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 $(C_2H_5)_2B(pyrazolyl)(C_7H_7)Mo(CO)_2$ in which, even at room temp-
erature, there is a definite interaction between the Mo atom and one of the
α 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 inter-
action could be strong enough to force the fragment to adopt the C_{4v} geometry
rather than some other. Thus this argues for a 'gas-phase' C_{4v} 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 char-
acterised compounds can be synthesised. Rest (15) first demonstrated that
photolysis of $Ni(CO)_4$ in N_2 leads to $Ni(CO)_3N_2$ 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 $N_2Mo(CO)_5$ (17);
photolysis in a mixed matrix of N_2/Ar causes generation of $N_2Mo(CO)_5$ 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:

$$N_2Mo(CO)_5 \;\underset{\text{432 nm}}{\overset{\text{367 nm}}{\rightleftharpoons}}\; Ar....Mo(CO)_5$$

367 nm   432 nm

$$Mo(CO)_6$$

To return to matrix mobility. Conclusive evidence for mobility of the carbonyl
intermediates comes from experiments on the matrix....$M(CO)_5$ and $N_2M(CO)_5$ 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 pol-
arized 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 I_{vert}
(contribution $\alpha \cos^2\theta$), I_{horiz} (contribution $\alpha \cos^2\phi$). Suppose there is a random
orientation of A molecules at the beginning, the nearer θ is to 90° for a par-
ticular 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
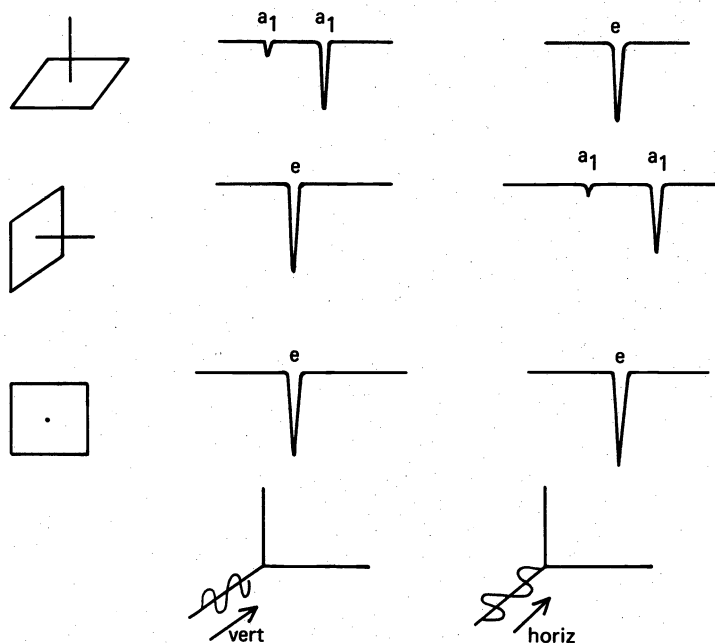metal carbonyls two examples will illustrate.

Fig. 5
Absorption probabilities of molecules

Photolysis   Analysis

vert   absorption $\propto \cos^2 \theta$

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

$$N_2Mo(CO)_5 \quad \xrightarrow[367 \text{ nm}]{h\nu \text{ pol}} \quad Ar\ldots.Mo(CO)_5$$

$$R \rightarrow 0 \qquad\qquad\qquad R$$

(R = random; 0 = 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,
$Ar\ldots.Mo(CO)_5$. Moreover reversal of the reaction:

$$Ar\ldots.Mo(CO)_5 \quad \xrightarrow[432 \text{ nm}]{h\nu \text{ pol}} \quad N_2Mo(CO)_5$$

$$R \rightarrow 0 \qquad\qquad\qquad R$$

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 hap-
pens to randomize the product.

This is even more strikingly demonstrated by our experiments on 'photoreorient-
ation', 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 $CH_4\ldots.Cr(CO)_5$, which illustrates the tech-
nique and provides photochemical information.

It is instructive to first note how the A_1 and E C-O stretching modes of differ-
ently 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 $CH_4\ldots.Cr(CO)_5$. On UV gen-
eration of $CH_4\ldots.Cr(CO)_5$ from $Cr(CO)_6$ the 'vert' and 'horiz' spectra have the
same intensity (not illustrated). On visible ($\lambda > 375$ 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 ret-
urned 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:

$$CH_4\ldots.Cr(CO)_5 \quad + \quad CO \quad \xrightarrow{h\nu \text{ pol}} \quad Cr(CO)_6$$

$$R \rightarrow 0 \qquad\qquad\qquad\qquad\qquad \text{(necessarily isotropic)}$$

Fig. 6
Activity in plane polarized light
of a_1 and e i.r. bands of square
pyramidal $M(CO)_5$ in three
extreme orientations.

However the net gain in the intensity of the visible band with vertical polar-
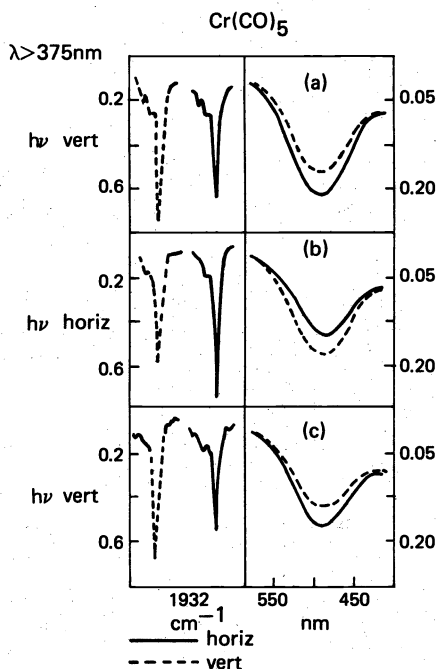ization on going from a) $\longrightarrow$ b) cannot be accounted for by simple photodepletion.

Fig. 7
Results of irradiation with
polarised light ($\lambda > 375$nm)
of $Cr(CO)_5$ isolated in a CH_4
matrix. (see also ref.19)

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 schemat-
ically represented for two orientations:
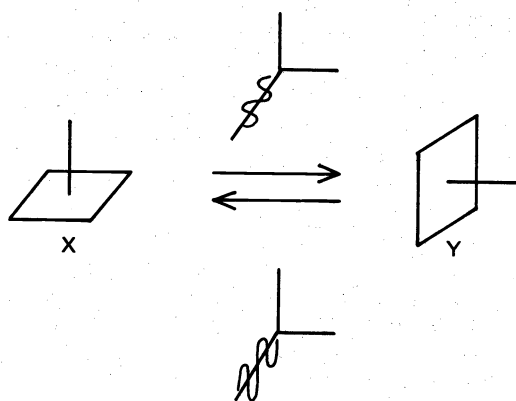
We do not of course know how far each molecule rotates on absorption of a
photon. The diagram simply illustrates that, as the photolysis proceeds, X → Y
after perhaps several photon absorptions. Once a molecule is in orientation
Y it is 'blind' to polarizing $h\nu_{horiz}$ radiation. Reversing the orientation
of polarized photolysis will build up the concentration of X. In theory
photolysis should proceed until <u>all</u> molecules are in orientation Y (or X)
and the dichroic ratio is infinite. In practice, for reasons discussed else-
where (23) this is never achieved but ratios of I_{vert}/I_{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 <u>during</u> 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 Ar....Cr(CO)$_5$ or N$_2$Cr(CO)$_5$ are expected to eject the 'ligand' on absorption
of visible radiation. Thus it is 'naked' Cr(CO)$_5$ that is being reoriented in the
matrix. There are two obvious mechanisms for this reorientation , a simple rot-
ation or a specific intramolecular rearrangement. That the latter is more likely
is shown by experiments on thiocarbonyl (CS) species where the CS group acts in
many ways like a labelled CO group. In particular, Ar....Cr(CO)$_4$CS generated by
UV photolysis of Cr(CO)$_5$CS shows wavelength dependent isomerism (24).
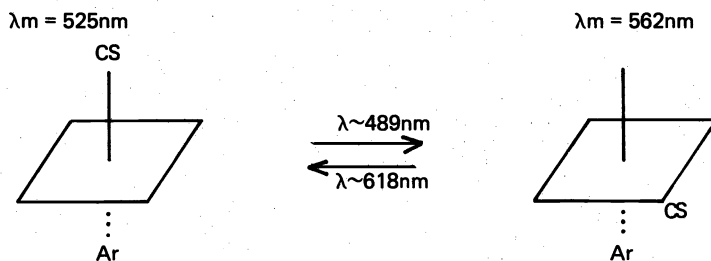
The most probable pathway for this rearrangement and for the reorientation of
Cr(CO)$_5$ is via a   trigonal bipyramidal intermediate configuration. EHMO cal-
culations (25) underscore this interpretation and the mechanism can be schemat-
ically represented for the naked Cr(CO)$_5$ as in figure 8.

Irradiation of matrix....Cr(CO)$_5$ with visible light results in ejection of the
matrix species and formation of naked Cr(CO)$_5$ in the excited state ^{1}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_{4v} configuration
relaxes to the D_{3h} structure which returns to the C_{4v} ($^1A_1$) ground state with
the same or a different orientation from the original matrix....Cr(CO)$_5$ molecule.
The overall mechanism is the square pyramidal analogue of the Berry process.
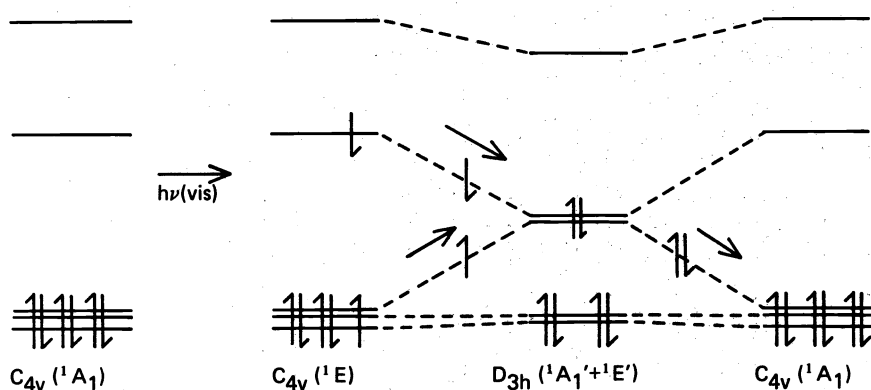We can represent the interchange by a correlation diagram:

$$C_{4v}\,(^1A_1) \qquad C_{4v}\,(^1E) \qquad D_{3h}\,(^1A_1{}'+{}^1E') \qquad C_{4v}\,(^1A_1)$$

Figure 8, which is strongly reminiscent of the Renner-Teller model for NH_2 (26)
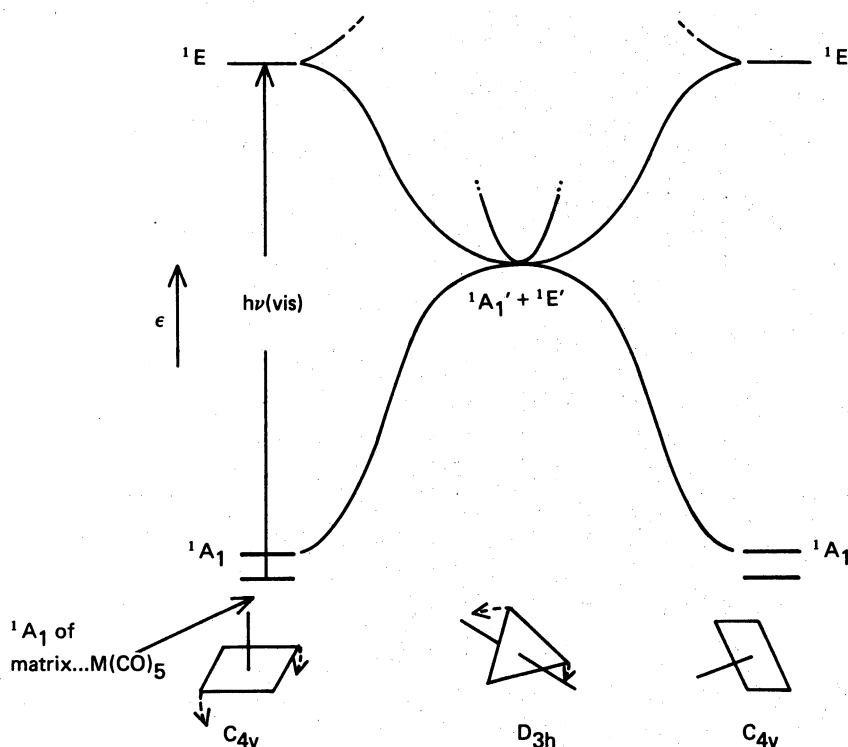provides a ready method for photoreorientation.

Fig. 8
Energy diagram for the ground and first excited singlet states of a d^6 $M(CO)_5$ fragment.
A slice through the potential energy surface connecting square pyramidal and trigonal
bipyramidal geometries.

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 '$M(CO)_5$', including
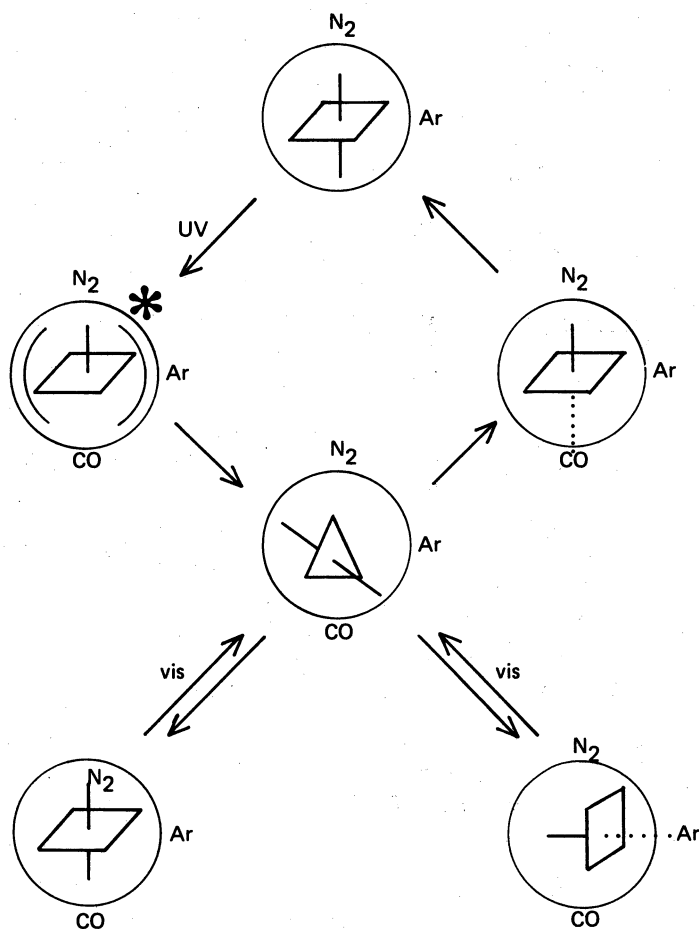   the reversal to $M(CO)_6$ described at the beginning. This is shown in
      figure 9.

Fig. 9
Photochemical behaviour of
'M(CO)$_5$' in a mixed N$_2$/Ar
matrix via a trigonal
bipyramidal intermediate.

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.

($\ast$ = ^{13}CO)
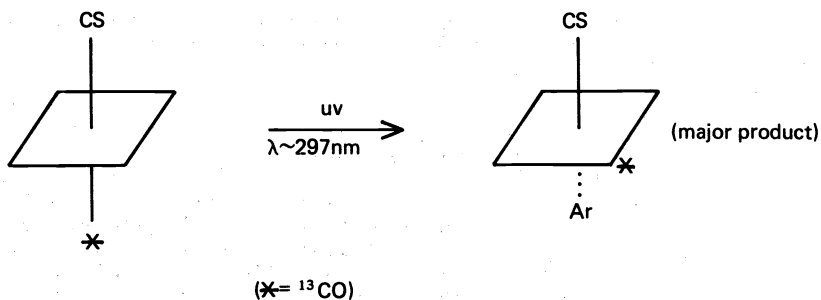
Irradiation into the visible band of Ar....Cr(CO)$_5$ gives excited C$_{4v}$ Cr(CO)$_5$, then D$_{3h}$ Cr(CO)$_5$ and then ground state C$_{4v}$ Cr(CO)$_5$ with again several possible orientations. If the empty site faces CO we have regenerated Cr(CO)$_6$. If the

empty site faces an argon atom Ar....$Cr(CO)_5$ is reformed, and can be photolysed again. If it faces an N_2 molecule we form $N_2Cr(CO)_5$ which does not absorb at the frequency used and there is therefore overall conversion of Ar....$Cr(CO)_5$ to $N_2Cr(CO)_5$. 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 now 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 C_{4v} structure; this will very rapidly rearrange via the D_{3h} configuration to the C_{4v} 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 $C_{4v} \rightarrow D_{3h} \rightarrow C_{4v}$ 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 CH_4.... $Cr(CO)_5$ at 20K, a weak cyclohexane (solv)....$Cr(CO)_5$ complex is expected. At room temperature an equilibrium will exist between naked and weakly complexed $Cr(CO)_5$.

$$K = \frac{[solv....Cr(CO)_5]}{[solv][Cr(CO)_5(n)]} \qquad (n \equiv naked)$$

Although the equilibrium constant is not expected to be very different from unity, the very large excess of cyclohexane (cyclohexane: carbonyl =10^5:1) 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 CH_4 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.

$$Rate = k[Cr(CO)_5(n)][CO] \qquad \text{(rate of recombination with CO)}$$

assuming, as seems reasonable, that the reaction proceeds via an SN_1 mechanism. Since $[Cr(CO)_5(n)]$ is low, the rate is relatively slow (cf. $Fe(CO)_4$ later).
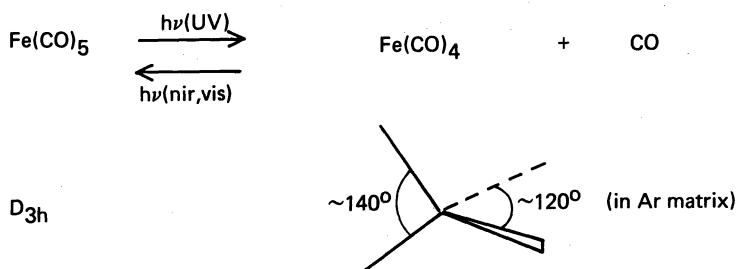
$$Rate = k\frac{[solv....Cr(CO)_5][CO]}{K[solv]}$$

From the matrix data we know that the interaction of $Cr(CO)_5$ with CH_4 or hydrocarbon/glass is greater than with CF_4. 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 cyc...$Cr(CO)_5$ > 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:

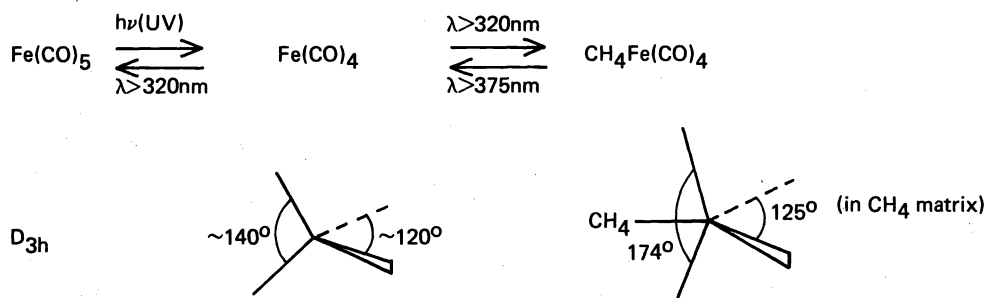| solvent	cyclohexane	C_7F_{14}
Rate constant ($1.mol^{-1} s^{-1}$) '$Cr(CO)_5$' + CO $\longrightarrow Cr(CO)_6$	3×10^6	3.5×10^8

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 <u>seven</u>-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.
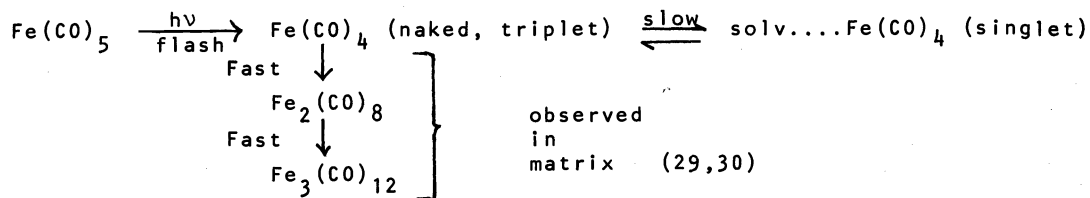
$$Fe(CO)_5 \; \underset{h\nu(nir,vis)}{\overset{h\nu(UV)}{\rightleftarrows}} \; Fe(CO)_4 \quad + \quad CO$$

D_{3h} ~140°   ~120°   (in Ar matrix)

In the argon matrix (also Ne) there is no evidence for any stereospecific argon/ $Fe(CO)_4$ interaction. With CH_4 (also xenon), <u>two</u> 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 CH_4 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.

$$Fe(CO)_5 \; \underset{\lambda>320nm}{\overset{h\nu(UV)}{\rightleftarrows}} \; Fe(CO)_4 \; \underset{\lambda>375nm}{\overset{\lambda>320nm}{\rightleftarrows}} \; CH_4Fe(CO)_4$$

D_{3h} ~140°   ~120° CH_4—174°   125°   (in CH₄ matrix)

All distorted tetrahedral d^8 complexes are paramagnetic (triplet) and all flat (square planar) d^8 complexes are diamagnetic (singlet). Molecular orbital calculations suggest that naked triplet $Fe(CO)_4$ has a C_{2v} structure with bond angles ~135°, ~110° close to those observed ~140°, ~120° and that the five-coordinate $CH_4Fe(CO)_4$ 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

$$Fe(CO)_5 \; \xrightarrow[\text{flash}]{h\nu} \; Fe(CO)_4 \text{ (naked, triplet)} \; \overset{slow}{\rightleftarrows} \; solv....Fe(CO)_4 \text{ (singlet)}$$

Fast ↓

$Fe_2(CO)_8$

Fast ↓   observed in matrix   (29,30)

$Fe_3(CO)_{12}$

During the flash $Fe(CO)_5$ is converted to $Fe(CO)_4$: this reacts very rapidly with itself through $Fe_2(CO)_8$ to $Fe_3(CO)_{12}$. 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 $Fe(CO)_4$ <u>appears</u> to be more reactive than $Cr(CO)_5$ in flash photolysis experiments may be that naked $Fe(CO)_4$ is in fact <u>less</u> 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 <u>pure CO matrix</u> gives $Cr(CO)_5$ (31). Similarly $Fe(CO)_4$ 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 $\underset{|}{C}O....Cr(CO)_5$, 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....$Cr(CO)_5$ <u>does</u> thermally reverse
to $Cr(CO)_6$ on warming the matrix but CO....$Cr(CO)_5$ does <u>not</u>. The different
behaviour with Ar and CO as 'ligand' is gratifyingly in line with the conclus-
ions 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 photo-
reoriented 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,

	CH_4	Ar	CO
$\dfrac{\phi_{vis}}{\phi_{UV}}$	0.04	0.2	6

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 character-
ize $Cr(CO)_5$ 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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