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Photochemistry of the Group 6 Hexacarbonyls in Low-Temperature Matrices. III.[1,2] Interaction of the Pentacarbonyls with Noble Gases and Other Matrices

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Abstract: $Cr(CO)_5$, $Mo(CO)_5$, and $W(CO)_5$ may be generated in a variety of matrices by uv photolysis of $M(CO)_6$. The visible absorption band of the pentacarbonyls is extremely sensitive to the matrix (Cr-Ne 624 nm, Cr-Xe 490 nm). Mixed matrix experiments and comparison with spectra of stable species show that the shift in the visible band is due to stereospecific interaction between $M(CO)_5$ and the matrix species occupying the sixth coordination site. In the mixed matrices the different $M(CO)_5$-matrix species can be interconverted photochemically. The changes in the spectra reveal differences in the frequency and intensity of the ir bands of the $M(CO)_5$-matrix species, which indicate a significant change in bond angle between different $M(CO)_5$-noble gas species in the same matrix. The shifts in the visible band are interpreted in terms of a weak metal-matrix bond and the effect of this change in angle. The implications for solution and matrix photochemistry are discussed.

Organometallic intermediates, particularly simple carbonyls of the transition metals, are receiving increasing attention. Such intermediates (e.g., $Cr(CO)_5$) have been examined by conventional solution flash photolysis which allows kinetic measurements to be made if the intermediate uv-visible spectrum can be assigned.[3] Alternatively the intermediate can be generated photochemically and trapped in a low-temperature solid matrix which permits examination of *both* vibrational and electronic spectra.[1] It is often relatively easy, particularly with the aid of isotopes, to prove (by vibrational spectroscopy) the structure of a trapped fragment; e.g., $Cr(CO)_5$ has been shown to be square pyramidal.[2] In principle the matrix uv-visible data of the fragment can then be used to aid interpretation of the solution flash work. This extrapolation assumes that the spectroscopic properties in the two environments will be very similar, provided that the structures in solution and matrix are the same. For stable compounds, where comparison is easy, it is generally found that vibrational frequency shifts are small but that there can be modest effects[4] on uv-visible spectra.

Kelly et al. have shown that flashing $Cr(CO)_6$ in very pure cyclohexane solution produces a transient absorption at 503 nm;[3b] this band is assigned to $Cr(CO)_5$ and is extremely sensitive to impurities, presumably because of the possibility of complex formation. On the other hand $Cr(CO)_5$ generated in low-temperature matrices has a band at 489 nm in methane[5] and 533 nm in argon.[1] This discrepancy, which led us originally to speculate on possible formation of $Cr(CO)_5$-CH_4 in the matrix and hence $Cr(CO)_5$-cyclohexane in solution,[5] has led to a systematic investigation of the spectroscopic properties of the fragment in a wide variety of matrices.

The results show that both the C-O stretching vibrations and the visible absorption bands of $M(CO)_5$ are subject to stereospecific effects due to interaction of the carbonyl with the matrix species in its vacant site. This interaction causes the $M(CO)_5$ visible absorption to be exceptionally sensitive to the matrix. The effects on the ir spectrum are normally obscured by "solvent" effects similar to those observed for $M(CO)_6$, but can be unmasked by using mixed matrices.

The mixed matrices also reveal the rich photochemistry of the matrix-$M(CO)_5$ species. Indeed the different spectroscopic and photochemical properties suggest that these species are distinct chemical entities. In the light of these peculiar results the assumptions of similar spectroscopic properties in matrix solution and gas phase have been questioned, and new insights obtained into the properties of the carbonyl fragments.

Experimental Section

The earlier experiments were performed at 20°K on an Air Products AC-3L cryotip with hydrogen as the coolant. A few experiments with Ne matrices used helium in addition (4°K). Later experiments used a Displex CS-202 fitted with automatic temperature controller for 20°K experiments and an Air Products LT3-110 liquid transfer tube for 4°K experiments. Ir spectra were recorded on a Grubb Parsons Spectromajor modified to give improved performance in the region from 1800 to 2000 cm^{-1}. The

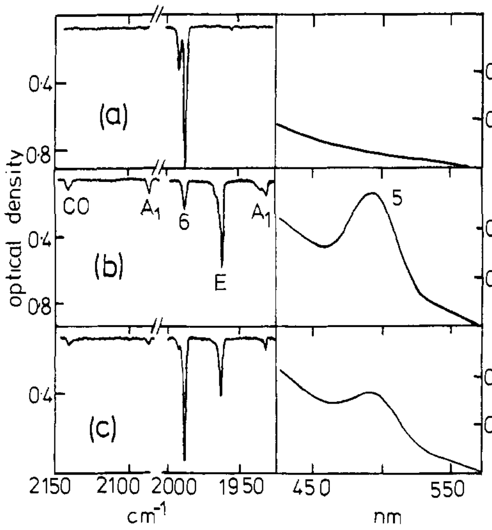


Figure 1. Photolysis of $Cr(CO)_6$ in CH_4 at 20°K (ir and visible spectra): (a) deposition of $Cr(CO)_6$ (T_{1u} mode marked 6); (b) 15 sec photolysis with unfiltered Hg arc showing production of $Cr(CO)_5$ and molecular CO; $Cr(CO)_5$ has three ir bands (marked A_1, A_1, and E) and a visible band (marked 5); the uv band of $Cr(CO)_5$ is not shown; (c) 2 min photolysis with Hg arc + λ >375 nm filter, showing regeneration of $Cr(CO)_6$. The spectra above 2050 cm^{-1} and the visible spectra are taken with about five times as much material as the spectra below 2050 cm^{-1}.

spectrometer was calibrated in this region with DCl, DBr, or inverse water peaks; below 700 cm^{-1} it was calibrated with CO_2. Quoted frequencies should be accurate to ±0.5 cm^{-1}. Uv-visible spectra were recorded on a Perkin-Elmer 356 spectrometer with a specially designed sample compartment.[6] The instrument was calibrated with a holmium filter. Any scatter was subtracted graphically. The wavelengths should be accurate to ±2 nm except in cases of very severe scatter (±4 nm). The shroud design for using this instrument has been described elsewhere,[6] as have the advantages of this spectrometer for matrix spectra.

Carbonyls were obtained from BDH and used without further purification; matrix gases were obtained from BOC (Grade X) except for SF_6 and CF_4 (Cambrian Gases). The matrices containing hexacarbonyls were deposited by pulsing[7] using a volume of 30 ml except for a Ne matrix (5 ml). $Cr(CO)_5NH_3$ was deposited by slowly subliming the room-temperature vapor and cocondensing with matrix gas. The usual mole ratios of matrix gas to hexacarbonyl were 2500:1.

The short wavelength photolysis source was either a medium pressure Hg arc with a water filter to remove heat or a cadmium lamp (Phillips) which has a strong emission at 229 nm. The long wavelength source was either the Hg arc used with a filter cutting off shorter wavelengths than 375 nm (Calflex C) or the Nernst glower of the ir spectrometer. At all other times the Nernst glower was covered by a filter to remove near ir and visible light. In early experiments an interference filter was used, but it was replaced later by a Ge filter which gave a flat background down to 550 cm^{-1}. The "tail photolysis" experiments used Balzer's interference filters which have a band-pass of about 20 nm (λ = 432 and 586 nm). Visible radiation was removed with a $CoSO_4/NiSO_4$ filter[8] leaving a useful range of $230 < \lambda < 340$ nm.

Results

1. Vibrational Spectra of $M(CO)_5$ in Low-Temperature Matrices. The pentacarbonyl fragment is readily generated by short wavelength photolysis of $Cr(CO)_6$ isolated in a low-temperature matrix. Figure 1a shows a typical ir spectrum in the C-O stretching region. The matrix splittings of the T_{1u} band of $Cr(CO)_6$ have been discussed previously.[1] $Cr(CO)_5$ (Figure 1b) is converted back to $Cr(CO)_6$ on long wavelength photolysis (Figure 1c). That the fragment has C_{4v} symmetry is suggested from the CO band pattern (A_1 2088, E 1961, A_1 1932 cm^{-1} in a CH_4 matrix) and is confirmed by detailed isotopic studies for both Ar and CH_4 matrices.[2]

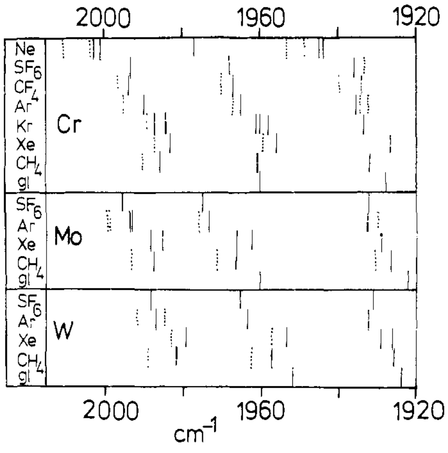


Figure 2. Diagrammatic representation of ir spectra of $M(CO)_6$ and $M(CO)_5$ in different matrices (gl = glass)[29]. For each matrix, the three groups of bands represent, from high to low frequency, $M(CO)_6$-T_{1u}, $M(CO)_5$-E, and $M(CO)_5$-A_1 modes, respectively. The dotted lines represent weaker components of the bands.

Table I. Separation between the Most Intense Component of the $M(CO)_6$ T_{1u} Mode and the Most Intense Component of the $M(CO)_5$ E Mode[a] (M = Cr, Mo, W)

	$\bar{\nu}_{T_{1u}}(M(CO)_6) - \bar{\nu}_E(M(CO)_5)$, cm^{-1}		
Matrix	Cr	Mo	W
Ne	25.0*		
SF_6	25.0	20.0	23.2
CF_4	23.8		
Ar	24.8	20.0	23.5
Kr	25.9*		
Xe	26.9	22.5*	26.0
CH_4	25.0	20.5	24.4

[a] Error = 0.4 cm^{-1} unless marked by an asterisk which indicates that this method did not give unique assignment because several bands were equally intense.

Comparison of spectral behavior between matrices is complicated by band splittings due to slight distortions and/or site effects (see below). However, Figure 2 shows schematically the positions of the ir bands of $M(CO)_6$ and $M(CO)_5$ (M = Cr, Mo, W) in a variety of matrices. The bands are sensitive to matrix but both hexacarbonyls and pentacarbonyls are similarly affected. Table I compares the separation of the most intense component of the $M(CO)_6$ T_{1u} mode with the most intense component of the $M(CO)_5$ E mode as a function of matrix. The constancy of these separations indicates that most of the perturbing effect of the matrix on the vibrational spectra is a general one. This method sets an upper limit of about 3 cm^{-1} on any stereospecific interaction between $Cr(CO)_5$ and the matrix species in its vacant site. (Large general "solvent" effects have also been observed for $Fe(CO)_4$ and $Fe(CO)_5$.[9])

In part II we discussed methods of calculating bond angles from intensity data and showed that the axial-radial bond angles of $Cr(CO)_5$ were 94.1° and 92.8° for Ar and CH_4 matrices, respectively. The intensity ratios of the bands were significantly different in these two matrices, but the difference in bond angles was within the experimental error (±1.8°). The measurement of the intensity ratios in other matrices was rather less accurate than in CH_4 and Ar matrices, because of uncertainty in the assignment of the tetracarbonyl bands (see below) and because fewer measurements were made. In most of these cases the high frequency A_1 was not observed because of the difficulty in ob-

Table II. Comparison of the Visible Bands of $M(CO)_5$ (M = Cr, Mo, W)[a]

	Band maxima					
	$Cr(CO)_5$		$Mo(CO)_5$		$W(CO)_5$	
Matrix	nm	cm^{-1}	nm	cm^{-1}	nm	cm^{-1}
Ne	624	16,000				
SF_6	560	17,900	450	22,200	461	21,700
CF_4	547	18,300				
Ar	533	18,800	429	23,300	437	22,900
Kr	518	19,300				
Xe	492	20,300	413	24,200	417	24,000
CH_4	489	20,400	411	24,300	413	24,200

[a] Errors ±2 nm, all spectra corrected for background scatter.

Table III. The Uv Band of $Mo(CO)_5$ and $W(CO)_5$ (Errors ± 3 nm)

	Band maxima			
	$Mo(CO)_5$		$W(CO)_5$	
Matrix	nm	cm^{-1}	nm	cm^{-1}
SF_6			241	41,500
Ar	244	41,000	241	41,500
Xe	245	40,800	244	41,000
CH_4	247	40,500	244	41,000

Table IV.

(a) Comparison of Bands[a] of $Cr(CO)_6$, $Cr(CO)_5NH_3$, and $Cr(CO)_5$ in Matrices

	$Cr(CO)_6$			
Matrix	Band 1	Band 2	$Cr(CO)_5NH_3$ visible band	$Cr(CO)_5$ visible band
SF_6	43,300 (231)	35,700 (280)	23,600 (424)	17,900 (560)
Ar	44,300 (226)	36,100 (277)	23,800 (420)	18,800 (533)
CH_4	44,100 (227)	35,700 (280)	23,800 (421)	20,400 (489)

(b) $Cr(CO)_5NH_3$ in Solution[b]

Solvent	$\bar{\nu}_{max}$, cm^{-1}	λ_{max}, nm	Solvent	$\bar{\nu}_{max}$, cm^{-1}	λ_{max}, nm
C_6H_{12}	23,100	434	CH_3OH	24,500	409
CCl_4	23,300	429	C_5H_5N	24,600	407
$CHCl_3$	23,700	422	$(CH_3)_2CO$	24,600	407
C_6H_6	23,800	420	CH_3CN	24,600	407
Et_2O	24,200	414	DMF	24,800	403

[a] In cm^{-1}, nm in brackets. [b] Maximum difference = 1700 cm^{-1}.

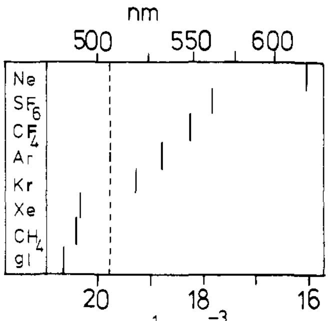


Figure 3. Diagrammatic representation of the visible band $Cr(CO)_5$ in different matrices (plot is linear in cm^{-1}): gl = glass,[29] broken line = value from flash photolysis of $Cr(CO)_6$ in cyclohexane solution.[3b]

taining large yields of pentacarbonyls without incurring very scattering matrices.

Bands below 1000 cm^{-1}. The spectrum of $Cr(CO)_5$ in the M-C stretching and M-C-O deformation region was studied in Ar and CH_4 matrices. The band positions differed by 2 cm^{-1} or less and their relative intensities were almost identical.

2. Uv-Visible Spectra of $M(CO)_5$. Figure 1b shows the visible absorption spectrum of $Cr(CO)_5$ in a CH_4 matrix. The assignment of the band to $Cr(CO)_5$ (and of similar bands to $Mo(CO)_5$ and $W(CO)_5$) follows from the growth and decay behavior of the uv-visible bands which match the ir band behavior (see Figure 1b). It should be noted that the comparisons between ir and uv-visible spectra are made in the same experiment on the same sample.

The $M(CO)_5$ uv-visible spectrum in the range 205-800 nm consists of two bands, the visible band of Figure 1b and a uv band at 230-250 nm which partially overlaps a band of the parent, $M(CO)_6$. This overlap is much more troublesome for $Cr(CO)_5$ than for $Mo(CO)_5$ and $W(CO)_5$, and has prevented any accurate measurement of the uv band position of $Cr(CO)_5$.

The position of the *visible* band of $M(CO)_5$ is extraordinarily sensitive to the matrix material used; it is much more sensitive than shifts commonly encountered in matrix or solution spectra, although all the matrices are nominally inert toward carbonyls. Table II summarizes the data and Figure 3 schematically shows the variation for $Cr(CO)_5$. The magnitudes of the shifts were similar in energy for all three carbonyls. When plotted against wavenumber, the bands in all matrices were slightly broader on the high-frequency side; half-widths ranged from 2600 to 3200 cm^{-1}.

Table III gives the corresponding data for the uv band for $Mo(CO)_5$ and $W(CO)_5$; in spite of the difficulties in measurement it is evident that this band is much less sensitive to matrix than the visible band.

To determine whether the shifts are due to a "generalized" solvent effect, as in the vibrational case, or due to a stereospecific interaction via the vacant coordination site, we need to compare the shifts with some other system. For a comparison to be valid we must ensure that we are looking at related electronic transitions.

The spectra of $LCr(CO)_5$ species [L = NH_3, RNH_2, R_2NH, R_3P] consist generally of one band near the visible and one or more stronger bands at shorter wavelength.[10] The latter are usually assigned to charge-transfer bands, but there has been considerable discussion about the correct assignment of the former; current opinion favors considerable d-d character.[10] We shall consider this problem in more detail later but in view of the similarity in spectra it is reasonable to assign the visible transition in $M(CO)_5$ to the same transition as the visible band in $LM(CO)_5$. On the other hand, the spectrum of $M(CO)_6$ is strikingly different. The two most intense bands are agreed to be CT bands; the d-d transitions, although detectable, are much weaker.[11] Thus although comparison with shifts in the $Cr(CO)_6$ spectrum is interesting there is not necessarily any connection with the behavior of $Cr(CO)_5$. Table IVa gives some data for $Cr(CO)_5NH_3$ and $Cr(CO)_6$ and the corresponding data for $Cr(CO)_5$. It is clear that whether compared with $Cr(CO)_5NH_3$ or $Cr(CO)_6$ the shift in the visible band of $Cr(CO)_5$ is very much larger. It is worth noting that the visible band of $Cr(CO)_5NH_3$ shows a sizable solvent shift in solution at room temperature (Table IVb). However, the frequency of the band maximum did not correlate well either with $(\epsilon - 1)(2\epsilon + 1)$ (ϵ = dielectric constant of solvent) or with Reichardt's E_T.[12] Even the magnitude of this solvent dependence is smaller than the matrix shifts of $Cr(CO)_5$.

This comparison suggests that the great sensitivity of the $M(CO)_5$ visible band is a consequence of the existence of the vacant coordination site. Further evidence for this conclusion comes from a study of the behavior of $Cr(CO)_5$ in *mixed* matrices.

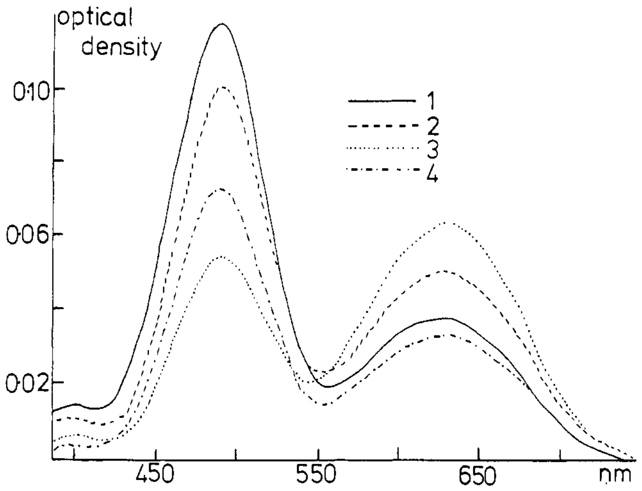


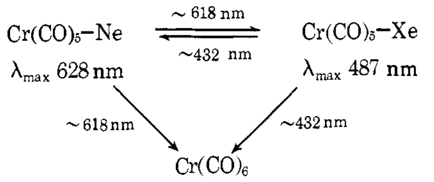
Figure 4. Visible spectra of $Cr(CO)_5$ in a Ne-2% Xe matrix at 4°K: (1) deposition of $Cr(CO)_6$ followed by 15 sec photolysis with unfiltered Hg arc; (2) 5 min photolysis with Hg arc + λ 432 nm filter; (3) 35 min further photolysis as (2). (4) 7 min photolysis with Hg arc + λ 618 nm filter.

3. Spectra of $Cr(CO)_5$ in Mixed Matrices. The behavior of spectral bands in mixed solvents has frequently been studied to help distinguish between general and specific solvent effects.[13] If the spectrum of a compound in a mixed solvent follows the weighted average of that in the pure solvents, this points to nonstereospecific effects. On the other hand, specific interaction is indicated by a strong preference for the spectrum obtained in one of the pure solvents, or the sum of the spectra observed in the pure compounds. Mixed matrices present similar possibilities with the added advantage that the solid state should give more control of the environment around the fragment.

The ir and visible bands of $Cr(CO)_5$ were studied as a function of photolysis time and wavelength in various mixed matrices. As uv photolysis proceeds the quantity of $Cr(CO)_5$ increases but the rate of increase slows down quite quickly. After long photolysis some $Cr(CO)_4$ is generated,[14] although in much lower yield than $Cr(CO)_5$. The visible band of $Cr(CO)_4$ is at about 400 nm and so does not interfere with the pentacarbonyl band. However, one of the ir bands of $Cr(CO)_4$ does overlap with the A_1 mode of $Cr(CO)_5$ preventing detailed examination of this region after long photolysis times.

Visible Band in Mixed Matrices. The two extreme positions of the visible band of $Cr(CO)_5$ in noble gas matrices are for Ne and Xe, making a Ne-Xe mixture the most suitable for these experiments. On initial photolysis at 4°K of $Cr(CO)_6$ in a Ne matrix doped with 2% Xe two well-resolved visible bands are observed (Figure 4, curve 1) centered at 628 and 487 nm (cf. $Cr(CO)_5$ in pure Ne 624 and in pure Xe 492 nm). The two bands have similar half-widths (cm^{-1}), but despite the small proportion of Xe, the short-wavelength component is much more intense than the long-wavelength component (see below). For simplicity we will refer to the long-wavelength component as $Cr(CO)_5$-Ne and the short-wavelength component as $Cr(CO)_5$-Xe.

Irradiation of $Cr(CO)_5$ in its visible band[1] in pure matrices results in recombination with CO to give $Cr(CO)_6$ (Figure 1). We should therefore be able to remove each component of the mixed matrix spectrum in turn by selective photolysis in one of the bands. Interference filters were chosen to coincide with lines of the Hg arc and the $Cr(CO)_5$ bands. Not only does photolysis in each component cause a *decrease* in its own intensity but also an *increase* in the other component (Figure 4). Comparison of traces 1 and 4 shows that the total quantity of $Cr(CO)_5$ has been reduced. Thus the following reactions are being observed.



This new reaction is analogous to ligand exchange in ordinary $XCr(CO)_5$ complexes; when $Cr(CO)_5$-A is photolyzed, either conversion to $Cr(CO)_5$-B or to $Cr(CO)_6$ represents a pathway to a complex which is unaffected by the incident radiation. (A and B represent the components of the mixed matrix.)

In a similar experiment with Ne doped with 2% Ar, white light photolysis generated $Cr(CO)_5$ with an absorption at 530 nm corresponding to $Cr(CO)_5$-Ar and a shoulder to long wavelength at the $Cr(CO)_5$-Ne position. No mixtures containing small proportions of Ne in Ar or Xe were tried because it was anticipated that Ne would diffuse readily in these matrices. However, a large number of experiments were performed with Ar doped with Xe or CH_4, and with CH_4 doped with Ar (Table V).

On initial photolysis of a 98% Ar-2% Xe mixture with the unfiltered Hg arc, a single band was observed at 522 nm, but on extended photolysis, the band maximum moved to 493 nm (Table V, experiment 1); i.e., the band maximum at first is close to $Cr(CO)_5$ in pure Ar but then moves to a position close to $Cr(CO)_5$ in pure Xe. Very similar behavior was observed for mixtures containing 98% Ar and 2% CH_4 (Table V, experiment 6). In neither experiment (Table V) were any shoulders observed on the bands, but they were often considerably broader than in the pure matrix and highly asymmetrical. Detailed examination with a curve resolver demonstrated that this behavior was characteristic of two bands, one at the pure Ar position and the other at the pure Xe (or CH_4) position whose relative intensities changed with photolysis time, thus giving rise to a shift in the band maximum. Simulation of this situation showed that no shoulders are expected to be discernible with such broad bands at this separation (Figure 5c). This resolution of two bands in the Ar-Xe mixtures exactly parallels the Ne-Xe results.

The method of selective visible photolysis described for the Ne-Xe mixtures should also provide a method of shifting the band maximum of the Ar-Xe mixtures. For these experiments, filters were used corresponding to the tails of the band in order to maximize the difference between its two components. Using this "tail-photolysis" method, the band could readily be moved in either direction (Table V, experiment 3). On photolysis in the short-wavelength tail, the band maximum moves to longer wavelength and vice versa; the process may be repeated several times (Figure 5a). After each photolysis there was a decrease in the total $Cr(CO)_5$ intensity, but close examination of Figure 5a shows that there is more $Cr(CO)_5$-Xe in trace 3 than in 2; in trace 4 there is more $Cr(CO)_5$-Ar than in trace 3. Thus "ligand exchange" is observed in this mixture as in the Ne-Xe mixtures. Again Ar-CH_4 mixtures behaved similarly.

An experiment (Table V, experiment 2) in which the Ar-Xe mixture was photolyzed with visible light from the Hg arc (λ >375 nm) serves as a control for the previous experiment. Now the band moves to higher frequency with progressive photolysis (Figure 5b) but each spectrum fits inside the envelope of the previous one. In this experiment, $Cr(CO)_5$-Ar is being reversed faster than $Cr(CO)_5$-Xe but

Table V. Summary of Data on $Cr(CO)_5$ Visible Band in Ar–Xe and Ar–CH_4 Mixed Matrices[c]

Experiment no, and matrix	Initial $Cr(CO)_5$ generation[a]	Subsequent photolysis			
1. Ar–2% Xe	0.25	White uv–visible	2.5	10	30
	522	photolysis	511	504	493
2. Ar–2% Xe	0.67	White visible	0.33	3	3
	519	photolysis	509	500	498
		($\lambda > 375$ nm)			
3. Ar–2% Xe	1.5	Tail photolysis[b]	30	30	30
	515	at λ shown	λ 586 nm	λ 432 nm	λ 586 nm
			490	522	491
4. Ar–2% Xe	1.33	Uv photolysis	42	40	20
	525	($CoSO_4$–$NiSO_4$)	Co–Ni	λ 586 nm	Co–Ni
		+ tail photolysis	522	495	524
5. Ar–10% CH_4	0.5	White uv–visible	0.5	5	Anneal
	507	photolysis and	503	498	494
		annealing			
6. Ar–2% CH_4	0.5	White uv–visible	Anneal	5	11
	526	photolysis and	528	522	502
		annealing			
7. Ar–1% CH_4	0.17	White uv–visible	1.67	5	61.5
	526	photolysis	524	519	518

[a] The H_2O filtered Hg arc was employed throughout. For initial generation no other filters were used except in experiment 4 where a $CoSO_4$–$NiSO_4$ filter ($230 < \lambda < 340$ nm) was used. [b] Ar–2% CH_4 behaved similarly on tail photolysis. [c] For experiments 1–7, the upper row shows photolysis times in minutes and the lower row shows the visible absorption maximum in nm.

the two species are not interconverted. The reason for the faster removal of $Cr(CO)_5$–Ar probably lies in the different intensities of the Hg arc lines and the different extinction coefficients of the $Cr(CO)_5$–Ar and $Cr(CO)_5$–Xe at the appropriate wavelengths. It should be noted that no isosbestic points were observed in any of these experiments because both the $[Cr(CO)_5\text{–}A]/[Cr(CO)_5\text{–}B]$ and the $[Cr(CO)_5]/[Cr(CO)_6]$ ratios changed simultaneously.

No significant differences in the uv band of $Cr(CO)_5$ between matrices could be observed because of the overlap with $Cr(CO)_6$ bands. However, insight into possible differences could be obtained using mixed matrices. When $Cr(CO)_5$ is generated using a $CoSO_4$-$NiSO_4$ filter to remove visible radiation ($230 < \lambda < 340$ nm) (Table V, experiment 4), the visible band maximum in an Ar-2% Xe matrix is at 525 nm and remains there on extended photolysis. However, if it is shifted to 490 nm using tail photolysis and then photolyzed again with the $CoSO_4$-$NiSO_4$ filter, it moves back to 525 nm. This movement strongly suggests that there are differences in the uv band of $Cr(CO)_5$-Xe and $Cr(CO)_5$-Ar in addition to the differences in the visible band already discussed. Attempts to shift the band in the opposite direction using monochromatic uv radiation were not successful.

The effect of varying the proportion of doping material was examined using Ar-CH_4 mixtures (Table V, experiments 5-7). Movements of the visible band were still observed with 1% CH_4 but not with 0.5% CH_4 even when extended photolysis with the unfiltered Hg arc was employed. In mixtures containing 10% CH_4, the band maximum was found closer to the pure CH_4 position than in the 2% mixture on initial photolysis (Table V). It is interesting that the band moved toward the CH_4 position on annealing this matrix, whereas no effect was found on annealing a 2% CH_4 mixture. The effect of reversing the proportions of the mixture (i.e., 90% CH_4-10% Ar) was tested using both extended uv-visible photolysis and tail photolysis. In neither case was any movement of the band observed. The only possible reason for this surprising behavior seems to be the overwhelming concentration of CH_4, giving only $Cr(CO)_5$-CH_4.

Ir Bands in Mixed Matrices. Under low resolution the ir spectra in all the mixed matrices show the usual three bands for $Cr(CO)_5$ corresponding to the E and A_1 modes. The mixed matrix has the effect of broadening all the bands because of the averaging of the inhomogeneous environment, so that most matrix splittings are removed. The frequencies invariably lie close to those observed for the pure major component of the mixture (Table VI), but under high resolution changes could be seen in the band profile corresponding to the movement of the visible band (Figure 6).

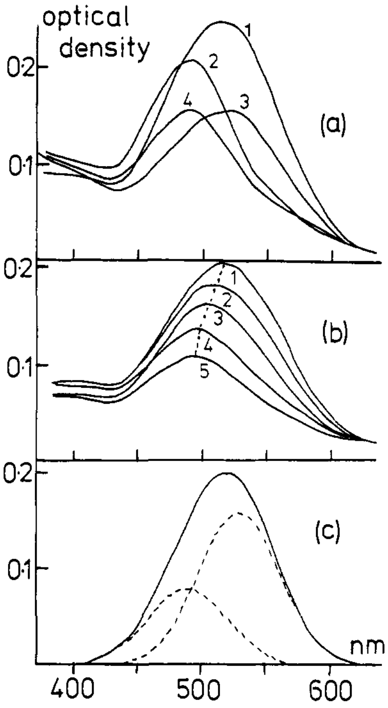


Figure 5. Visible spectra of $Cr(CO)_5$ in an Ar-2% Xe matrix at 20°K. (a) The effects of "tail photolysis": (1) deposition of $Cr(CO)_6$ followed by 1.5 min photolysis with unfiltered Hg arc; (2) 30 min with Hg arc + λ 586 nm filter; (3) 30 min with Hg arc + λ 432 nm filter; (4) 30 min as (2). (b) The effects of "white" visible photolysis: (1) deposition of $Cr(CO)_6$ followed by 40 sec photolysis with unfiltered Hg arc; further photolysis with Hg arc + $\lambda > 375$ nm filter for (2) 20 sec, (3) 50 sec, (4) 120 sec, (5) 180 sec. (c) Diagram of two Gaussians (broken lines) with positions and intensities corresponding to the spectra of $Cr(CO)_5$ in pure Ar and pure Xe. Solid line shows their sum.

Table VI. Mixed Matrix Data, Correlated Bands of $Cr(CO)_5-L$ (L = matrix species)[a]

Matrix	Ir bands, cm^{-1} E	Ir bands, cm^{-1} Low-freq A_1	Ir bands, cm^{-1} High-freq A_1	Visible band, nm	Assignment	Comments
Ne–2% Xe	1971	1933		628	$Cr(CO)_5-Ne$	
	1966	1943		487	$Cr(CO)_5-Xe$	
Ne–2% Ar				630 sh	$Cr(CO)_5-Ne$	Very high proportion of $Cr(CO)_5-Ar$
	1972	1941		533	$Cr(CO)_5-Ar$	No tail photolysis attempted
Ar–2% Xe	1964.5	1936.3	2092.4	525	$Cr(CO)_5-Ar$	
	1962.9	1939.1	2088.6	490	$Cr(CO)_5-Xe$	
Ar–2% CH_4	1964.9	1934.8		525	$Cr(CO)_5-Ar$	
	1964.3	1937.7		490	$Cr(CO)_5-CH_4$	
CH_4–10% Ar	1961	1933		491	$Cr(CO)_5-CH_4$	No $Cr(CO)_5-Ar$ observed

[a] Pairs of bands bracketed together are poorly resolved.

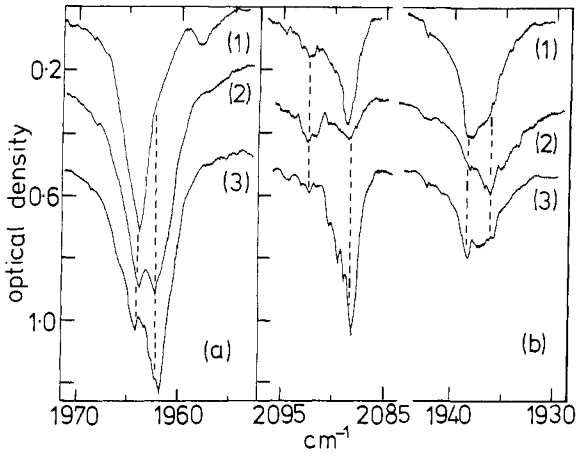


Figure 6. Ir spectra of $Cr(CO)_5$ in an Ar-2% Xe matrix at 20°K. Spectra are shown from different experiments because of the different extinction coefficients of the bands. (a) Spectra of the E mode. Corresponding visible absorption maxima in brackets: (1) 15 sec photolysis with unfiltered Hg arc (518 nm); (2) 43 min as (1) (493 nm); (3) 20 min with Hg arc + λ 586 nm filter (490 nm). (b) Spectra of the A_1 modes (extended photolysis is not applicable because of $Cr(CO)_4$ formation): (1) 1 min photolysis with unfiltered Hg arc (for low-frequency band only, this was followed by 30 min with Hg arc + λ 586 nm only); (2) 30 min with Hg arc + λ 432 nm filter; (3) 30 min with Hg arc + λ 586 nm filter.

Table VII. Deductions from Ir Spectra of $Cr(CO)_5$ in Ar–2% Xe Matrix

(a) Force Constants (mdyn $Å^{-1}$)[a]

	k_1	k_2	$k_{cis}(ae)$	$k'_{cis}(ee)$	k_{tr}
$Cr(CO)_5-Ar$	15.40	16.20	0.383	0.306	0.613
$Cr(CO)_5-Xe$	15.44	16.16	0.375	0.300	0.599
Relative errors	±0.01	±0.01	±0.0005	±0.0005	±0.001

(b) Relative Intensities and Bond Angles[b]

	R_1	R_2	θ	μ_a'/μ_r'
$Cr(CO)_5-Ar$	0.022	3.4	95.5	1.07
$Cr(CO)_5-Xe$	0.090	3.4	91.3	1.13
Relative errors	20%	10%	±1	±0.07

[a] Definitions of force constants from ref 2. [b] θ = axial–radial bond angle in degrees. μ_a'/μ_r' = ratio of axial–radial bond moment derivatives. $R_1 = I_{A_1(high)}/I_{A_1(low)}$. $R_2 = I_E/I_{A_1(low)}$.

On inital photolysis of $Cr(CO)_6$ in Ar-2% Xe mixture the E mode of $Cr(CO)_5$ was a singlet of half-width 3 cm^{-1}; as photolysis proceeded it broadened until it split into two components separated by 1.5 cm^{-1}, while the $Cr(CO)_6$ remained unaffected. Tail photolysis allowed either of the components to be reduced preferentially. Simultaneous visible spectra demonstrated that the higher frequency component corresponded to $Cr(CO)_5$-Ar (i.e., the visible band was close to the pure Ar position) and the lower frequency component to $Cr(CO)_5$-Xe. Similar splittings were observed in the A_1 bands, and it could be shown using the same arguments that the two A_1's of $Cr(CO)_5$-Xe are closer to each other than those of $Cr(CO)_5$-Ar (Table VI).

CO-factored force constants for the two species were calculated making the assumption that $\frac{1}{2}k_{trans} = k_{cis}(eq\text{-}eq) = 0.8k_{cis}(ax\text{-}eq)$ based on the complete force constants for $Cr(CO)_5$ in Ar calculated earlier.[2] The force constants (Table VIIa) are very similar, but the increase in k_1 and decrease in k_2 from $Cr(CO)_5$-Ar to $Cr(CO)_5$-Xe is significant and reflects the differences in the spectra of the two species.

The changes in intensity of the high-frequency A_1 also gave some crucial information about the relative ir and visible extinction coefficients of $Cr(CO)_5$-Ar and $Cr(CO)_5$-Xe (Figure 6b). On photolysis in the Ar tail, the decrease in intensity of the $Cr(CO)_5$-Ar A_1 band was much smaller than the increase in the $Cr(CO)_5$-Xe band. On photolysis in the Xe tail, the $Cr(CO)_5$-Ar band grew much less than the $Cr(CO)_5$-Xe decreased. Since only two processes take place during tail photolysis, "ligand exchange" and generation of $Cr(CO)_6$, it follows that a minimum value for the relative extinction coefficients of the high-frequency A_1 bands can be found by comparing optical densities of the bands in successive spectra. In this way $\epsilon_{A_1(high)}(Cr(CO)_5\text{-}Xe)/\epsilon_{A_1(high)}(Cr(CO)_5\text{-}Ar)$ was found to be greater than 3.5. No reference need be made in this argument to any other bands.

Using the same spectra of the high-frequency A_1 and simultaneous visible spectra it can be deduced that the $\epsilon_{vis}(Cr(CO)_5\text{-}Xe)/\epsilon_{vis}(Cr(CO)_5\text{-}Ar) \simeq 2.3$. The larger extinction coefficient of $Cr(CO)_5$-Xe probably explains the reason for its greater intensity on initial photolysis of the Ne-Xe mixture (Figure 4, curve 1).

From these and other experiments a complete set of ir relative intensities could be built up for the Ar-Xe mixture. Bond angles were then calculated using the method of Braterman et al.[15] (Table VIIb). Using isotopic substitution we demonstrated in part II that the "in-phase" solution was the correct one and only this solution is listed here. These calculations show that the change in intensity of the high-frequency A_1 band from $Cr(CO)_5$-Ar to $Cr(CO)_5$-Xe is caused by a decrease of about 4° in the axial-radial bond angle.

The ir spectra in other mixtures were less informative. The separation of the two components of the E mode was greater in Ne-Xe than in Ar-Xe mixtures (Table VI), but they were less well resolved because they were so much broader. No splitting of the E mode was observed for Ar-CH_4 mixtures, but slight movements of the band maximum were detected.

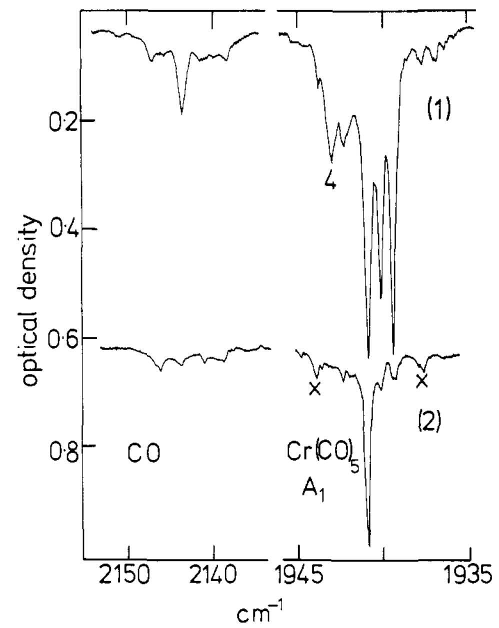


Figure 7. High-resolution spectra of low-frequency A_1 of $Cr(CO)_5$ and molecular CO in Ar at 20°K. Spectra are taken from different stages of an experiment because of the different extinction coefficients: (1) deposition of $Cr(CO)_6$ followed by 1 min photolysis with unfiltered Hg arc (a monochromator set at 300 nm was used for the molecular CO spectra to ensure a high yield without secondary photolysis); (2) 3 min with Hg arc + λ >375 nm filter.

The presence of two sets of bands in both the visible and ir spectra of $Cr(CO)_5$ in mixed matrices is further strong evidence of a stereospecific interaction of the matrix species in the vacant coordination site with $Cr(CO)_5$. This observation together with the photolysis behavior allows the possibility of fractional crystallization of the two components of the matrix to be excluded. However, other obvious objections to the interpretations required further experiments which are described below.

4. Some Further Experiments. (a) Effect of Dilution. It could be argued that the results are related to polymer formation in the matrix; the difficulty of ensuring that isolated monomers are examined has been much discussed in the past. In most of the experiments described here the molar ratio of hexacarbonyl to matrix was 1:2500. To ensure that the effects observed were not concentration dependent, experiments with argon or CH_4 matrices were performed at concentration of 1:10,000 and 1:50,000.

The ir and uv-visible bands assigned to $Cr(CO)_5$ behaved in precisely the same way as in the more concentrated matrices. In the 1:2500 $Cr(CO)_6$-argon experiments very weak ir bands are seen at 1977 cm^{-1} in the starting spectrum and at 2034 and 1993 cm^{-1} on prolonged photolysis.[8] At 1:10,000 these bands are even weaker and at 1:50,000 they are absent altogether. These bands can thus be assigned to traces of polymer; no corresponding bands could be detected in the uv-visible spectrum.

(b) Effect of Temperature. In argon and methane matrices the visible band has been studied at temperatures ranging from 4 to 40 and 11-40°K, respectively, without detecting any change in the band. Above 40°K the matrices boil off rapidly. In many cases the matrices were annealed without any effect on the ir or visible spectra except a sharpening of the ir bands. Thermal regeneration of $Cr(CO)_6$ was not observed unless there was excess CO in the matrix.

(c) Isocarbonyl-Type Structures. The reasons for rejecting $(OC)_5CrOC$ (with a strong Cr-O bond) as the photolysis product of $Cr(CO)_6$ in Ar matrices have been discussed earlier.[1,2] The possibility of weak interaction with the ejected CO via the vacant coordination site has also been refuted,[2] but the mixed matrix evidence makes the arguments against this structure even more compelling; it is impossible to reconcile the presence of two distinct visible bands with such a structure.

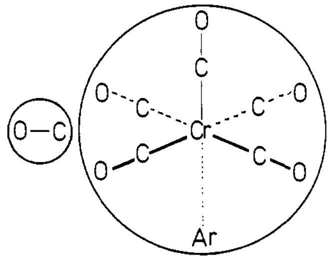


Figure 8. Diagram showing interaction of $Cr(CO)_5$ with Ar in the first coordination sphere and ejected CO in the second coordination sphere. The exact position of the ejected CO is arbitrary.

It should however be emphasized that it is possible to obtain a distinct $Cr(CO)_5$-CO species (λ_{max} 462 nm), where the CO is weakly interacting, by photolysis of $Cr(CO)_6$ in CO-doped matrices.[32]

Poliakoff and Turner,[9] in their paper on the photochemistry of $Fe(CO)_5$ in matrices, described changes in the spectrum of $Fe(CO)_4$ and CO on prolonged photolysis and on reversal to $Fe(CO)_5$. After brief uv photolysis of $Fe(CO)_5$ in argon the $Fe(CO)_4$ and CO generated recombine readily on long wavelength photolysis, but on prolonged uv photolysis recombination no longer occurs. For both $Fe(CO)_4$ and CO, the spectra of the "irreversible" and "reversible" molecules are distinct; the "reversible" bands are assigned to $Fe(CO)_4$ interacting with CO.

In part II, we mentioned that the splitting of the low-frequency A_1 band of $Cr(CO)_5$ in Ar and CH_4 matrices could be removed by brief long-wavelength photolysis, and in this paper we have also mentioned the splittings of this band. Indeed the behavior of this band and that of the molecular CO generated is similar to the behavior of $Fe(CO)_4$ and CO (Figure 7). Two components of the A_1 band reverse much more rapidly than the third. The changes may also be produced by prolonged photolysis, and are correlated with changes in the region of molecular CO. However, the CO spectra cannot be interpreted as simply as those from $Fe(CO)_5$ photolysis although it is clear that the 2141.5 cm^{-1} band reverses faster than the others. The splittings of the E mode are not as severe as those of the A_1 mode and cannot be removed by reversal.

In the previous discussion it was shown that under these conditions there is no interaction of the ejected CO with the vacant site of $Cr(CO)_5$. It therefore follows that the CO must initially occupy sites in the *second* coordination sphere of the metal atom (Figure 8). The splittings of the A_1 band represent $Cr(CO)_5$ with CO occupying different sites in the second coordination sphere. The sharpness of the bands (fwhm = 0.8 cm^{-1}) and reproducibility of the spectrum indicates that the ejected CO must occupy specific sites. This contrasts with the situation in a matrix doped with CO where random sites are occupied and the band is very broad.

These conclusions are entirely consistent with our earlier argument that the ir spectra of $Cr(CO)_5$ and $Cr(CO)_6$ are very sensitive to the enviromment in their second coordination sphere, but that the ir spectrum of $Cr(CO)_5$ is rather less sensitive to the occupant of its sixth coordination sites.

(d) Effect of Impurities. The level of impurities in the matrix gases is much too low to have any effect on the matrix isolated $M(CO)_5$ (see Experimental Section). Impurities

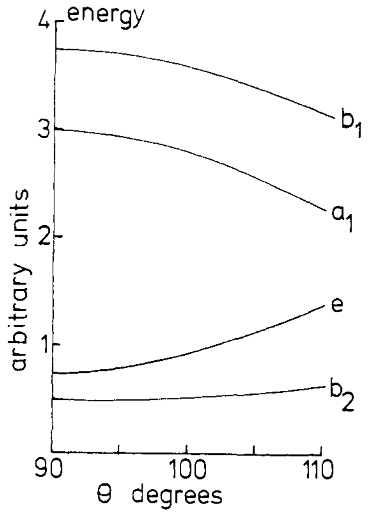


Figure 9. Graph of d orbital energies of a pentacarbonyl plotted against the axial-radial bond angle, θ, calculated by the perturbation method.[23] The change in energy with angle is significant but the absolute energies are not.

due to leaks in the apparatus could be N_2, O_2, CO_2, or H_2O. A substantial leak is well known[8] to give a characteristic band at 1975 cm^{-1} due to $Cr(CO)_5N_2$. H_2O can be detected by its effect on the CO spectrum;[7,16] $Mo(CO)_5{\cdot}H_2O$ has been characterized in glasses recently[17] and has a substantially different spectrum from $Mo(CO)_5$. No evidence for either N_2 or H_2O impurities was found in these experiments. The effect of small proportions of CO_2 or O_2 is less certain but it is unlikely that they would occur in the matrix without N_2 or H_2O. In pure CO_2 the visible band is at 418 nm; in pure O_2 no product was observed, prolonged photolysis resulting in destruction of starting species. At the pressures used during these experiments (10^{-7}-10^{-6} Torr) we may safely conclude that impurities are not responsible for any of the results described.

Discussion

The experiments described in the last section lend considerable support to the conclusions drawn from the mixed matrix experiments. In view of the complexity of some of the experiments, it is worth summarizing the results. (i) $Cr(CO)_5$ with C_{4v} symmetry is generated by white light photolysis of $Cr(CO)_6$ in a variety of matrices including CO. (ii) The visible absorption bnad of $Cr(CO)_5$ is extremely sensitive to the matrix (Ne 624-Xe 490 nm). This shift is due to the stereospecific interaction between $Cr(CO)_5$ and the species occupying the sixth coordination site. (iii) In a mixed matrix containing A and B, the visible spectra correspond to the sum of the spectra due to $Cr(CO)_5$ interacting with A and $Cr(CO)_5$ interacting with B. (iv) In all mixed matrices, except those containing 90% CH_4, $Cr(CO)_5$-A could be converted to $Cr(CO)_5$-B and vice versa using filtered photolysis. (v) There are corresponding changes in the ir spectra which show that the axial-radial bond angle in $Cr(CO)_5$-A differs from $Cr(CO)_5$-B. Even in dilute matrices, the ratio of, e.g., CH_4/$Cr(CO)_5$-CH_4 is very large so that any effect on the CH_4 vibrations is swamped by the spectrum of unperturbed CH_4.

We believe that these observations can only be interpreted by the following model. $Cr(CO)_5$ forms a weak bond with noble gases, SF_6, CF_4, and CH_4, which decreases in strength as the visible absorption band shifts to longer wavelength.

In an Ar matrix doped with 10% CH_4, the visible band of $Cr(CO)_5$ shifts readily on suitable photolysis, but in a CH_4 matrix doped with 10% Ar, no shifts are detectable at all. It follows from this observation that $Cr(CO)_5$-CH_4 is more stable than $Cr(CO)_5$-Ar. It also seems reasonable that $Cr(CO)_5$-Xe will be more stable than $Cr(CO)_5$-Ar or $Cr(CO)_5$-Ne. The difference in stability need not be directly related to the separation of the visible bands.

The shifts in the visible absorption maximum in the different matrices are greater than 4000 cm^{-1} or 25% whereas the stereospecific shifts in the ir spectrum are less than 5 cm^{-1} or 0.25%. It is of considerable interest to discuss the origins of these shifts, especially since the interaction energy between $Cr(CO)_5$ and say a Xe atom occupying its vacant site might be comparable in energy to a weak chemical bond (4-20 kJ mol = 350-1750 cm^{-1}).

Most authors have argued that the major visible transition $XM(CO)_5$ species is an $e \rightarrow a_1$ transition,[10,18] although they are not agreed on the proportion of charge-transfer character. We propose that the visible band of $M(CO)_5$ is due to the same symmetry allowed ${}^1A_1 \rightarrow {}^1E$ transition[19] ($b_2{}^2e^4a_1{}^0b_1{}^0 \rightarrow b_2{}^2e^3a_1{}^1b_1{}^0$), but it should be noted that recent calculations and interpretation of photoelectron spectra of such species suggest that one-electron models may be inappropriate because of the breakdown of Koopman's theorem.[20]

Most of the matrices used (e.g., Xe, CH_4, etc.) are very weak σ donors. They can affect the energy of the $e(d_{xz,yz})$ orbital only through increasing the overall charge on the metal, but they can interact directly with the a_1 metal orbital[21] (CO π^* and d_{z^2}; see Figure 2 of ref 21) raising it and at the same time donating electron density to the metal. Thus a weak M-Xe bond will increase the $e \rightarrow a_1$ one-electron transition energy, regardless of the proportion of charge-transfer character. The shifts in the uv-visible spectrum cannot be entirely attributed to the Cr-A (A = matrix species) bond energy. It seems unlikely that Franck-Condon factors could change so drastically from one matrix to another. Furthermore such changes would be expected to change the band shape significantly, but only very small changes are observed. Charge transfer to the matrix can be rejected because it would shift the band in the opposite direction from that observed.

An alternative possibility lies in the geometry of the molecule. Guenzburger et al.[22] and Burdett[23] have independently shown that the energies of the e and a_1 orbitals of the d manifold of C_{4v} complexes are sensitive to the axial-radial bond angle. As this angle increases, the energy of the e orbital rises slowly, while the a_1 orbital falls rapidly (Figure 9). A small increase in the axial-radial bond angle can generate a large decrease in the $e \rightarrow a_1$ energy. It would be expected that the bond angle might be slightly smaller with Xe in the sixth site than with Ne, making the $e \rightarrow a_1$ energy larger.

We have already demonstrated just such a change in the bond angle between $Cr(CO)_5$-Ar and $Cr(CO)_5$-Xe, both isolated in the same Ar-2% Xe matrix. Rather weaker evidence of a bond angle change between $Cr(CO)_5$ in pure CH_4 and Ar matrices was obtained earlier.[2]

The bond angle explanation is attractive as one of the chief causes of the shifts in the visible band. The bond angle in turn must be related to the size of the matrix species in the vacant site of $M(CO)_5$. However, the evidence from the molecular matrices shows that size is not the only factor which determines the position of the visible band. CH_4 and Xe appear similar as matrices, although they must differ considerably in size. The behavior of SF_6 and CF_4 can only be rationalized on a size argument if it is assumed that the fluorine atoms alone affect the bond angle.

We suggest, therefore, that the shifts in the visible band from one matrix to another are caused by a combination of two effects both working in the same direction: (a) the presence of a weak matrix species-metal bond and (b) a small change in the axial-radial bond angle determined by the matrix species in the sixth coordination site. Finally it should be pointed out that the interaction energy between metal and matrix need not be identical in the ground and excited states.

In contrast to the uv-visible spectrum, the solvent effects on the ir spectrum are very large ($\Delta\nu(\mathrm{Cr(CO)_6\text{-}T_{1u}})$ from Ne to Xe = 20 $\mathrm{cm^{-1}}$), and the stereospecific effects considerably smaller ($\Delta\nu_E(\mathrm{Ne\text{-}Xe})\mathrm{Cr(CO)_5}$ = 5 $\mathrm{cm^{-1}}$). Large solvent effects on the C-O stretching bands are well known. The smaller effect of stereospecific interactions are entirely consistent with the conclusions of Brown and Dobson[24] who examined the variations in the force constants of $\mathrm{LW(CO)_5}$ complexes with the $\mathrm{p}K_\mathrm{a}$ of the amine L. They found that "there is little effect of changes in ligand σ-bonding on carbonyl stretching frequencies either through interaction with the metallic π system or directly through changes in carbonyl to metal σ-bonding".

We have demonstrated that the different species $\mathrm{Cr(CO)_5}$-A (A = Ne, Xe, $\mathrm{CH_4}$, CO, $\mathrm{SF_6}$, etc.) are photochemically, geometrically, and spectroscopically distinct. Indeed, within the matrix context they behave exactly as expected for a complex $\mathrm{XM(CO)_5}$. Cotton et al. have recently discovered two complexes[25] containing a B-($\mathrm{H_2}$)C-H-Mo grouping and have shown that this bridge can compete with a metal-olefin bond. Hodges et al.[26] found good evidence for H-D exchange of alkanes catalyzed by platinum complexes. Fischer[27] has shown the high electronegativity of the $\mathrm{M(CO)_5}$ unit through his dipole moment measurements on metal pentacarbonylcarbene complexes. Breeze and Turner[28] have shown that the species $\mathrm{Cr(CO)_5^-}$ can be isolated in an Ar matrix by cocondensation of $\mathrm{Cr(CO)_6}$ and Na followed by photolysis. The dianions $\mathrm{M(CO)_5^{2-}}$ are indeed well known. We therefore feel that the M-A interaction in the $\mathrm{M(CO)_5}$-A species in the matrix may reasonably be described as a weak chemical bond even in such matrices as Ar.

The photochemical mechanism of reversal of $\mathrm{Cr(CO)_5}$ to $\mathrm{Cr(CO)_6}$ has already been discussed.[1] The evidence for apparent labilization of Ne in $\mathrm{Cr(CO)_5}$-Ne and subsequent conversion to $\mathrm{Cr(CO)_5}$-Xe raises new questions which cannot be answered entirely on the basis of the "thermal" mechanism proposed earlier.[1] In a future paper we will discuss some experiments using polarized photolysis and propose a mechanism for the photochemical observations described in this paper.

Implications for the General Use of Matrices Comparison with Flash Photolysis, Etc. Previous matrix isolation experiments have shown that the gas to matrix shifts in ir and uv spectra are relatively small,[4] implying that conclusions for one state are likely to be valid for the other state. Our results support this conclusion for molecules which are perturbed nonstereospecifically by the matrix. They show, however, that other molecules may interact substantially with matrix species normally expected to be inert. These stereospecific interactions are tantamount to the formation of a chemical bond. Under these circumstances the nearest spectrum to that in the gas phase must be in a neon matrix. It is reasonable to conclude that the C_{4v} state of the pentacarbonyl is stable in the gas phase, although it may not be the only or the most stable geometry. In the light of these experiments, matrix spectra of unstable molecules should be examined with great caution, although extensive investigations may yield new and unexpected properties. In this context the limitations of experiments in glasses are particularly apparent since the matrix material offers little scope for variation. Indeed the spectra of $\mathrm{Cr(CO)_5}$ in glasses[29] are now seen to be of $\mathrm{Cr(CO)_5}$-methylcyclohexane, a species similar to $\mathrm{Cr(CO)_5\text{-}CH_4}$.

Flash photolysis of $\mathrm{Cr(CO)_6}$ in cyclohexane solution results in the appearance of a band maximum[3b] at 503 nm whose lifetime and position are critically dependent on impurities in the solution. This position is reasonably consistent with the $\mathrm{CH_4}$ matrix value (489 nm) although a small discrepancy remains. Its sensitivity to impurities, particularly those containing oxygen, is entirely consistent with a C_{4v} pentacarbonyl.

The relatively long lifetime of $\mathrm{Cr(CO)_5}$ in solution is probably due to the complexation of the cyclohexane. Using our data Kelly predicted that the lifetime in fluorinated solvents should be much shorter and this has indeed been found.[30] However, the true identity of the flash intermediate cannot be confirmed without ir spectra.

The behavior of $\mathrm{Cr(CO)_5}$ makes an interesting comparison with that of $\mathrm{Fe(CO)_4}$. $\mathrm{Cr(CO)_5}$ is only observable in one C_{4v} form in any one pure matrix and appears always to be in the complexed form $\mathrm{Cr(CO)_5}$-A; in the mixed matrix the geometrical difference between different $\mathrm{Cr(CO)_5}$-A species is only slight. "Naked" C_{4v} $\mathrm{Cr(CO)_5}$ and $\mathrm{Cr(CO)_5}$-A should both have singlet ground states. $\mathrm{Fe(CO)_4}$ in Xe and $\mathrm{CH_4}$ matrices is found in two forms[31] which can be interconverted photochemically. In the "free" state $\mathrm{Fe(CO)_4}$ has C_{2v} geometry with bond angles of about 120 and 140° and is predicted to have a triplet ground state. The "complexed" form, $\mathrm{Fe(CO)_4CH_4}$, also has C_{2v} geometry but has bond angles of 174 and 125° and is predicted to have a singlet ground state. Presumably the large geometry change and the triplet to singlet interconversion provide a barrier to the complexation of $\mathrm{Fe(CO)_4}$. In $\mathrm{Cr(CO)_5}$ no such barrier exists and only the complexed form is observed.

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Photochemistry of the Group 6 Hexacarbonyls in Low-Temperature Matrices. IV.[1-3] Tetracarbonylmolybdenum and Tricarbonylmolybdenum

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Abstract: Uv photolysis of $Mo(CO)_6$ in a CH_4 matrix produces $Mo(CO)_5$ and two secondary photolysis products, which grow sequentially. Their spectra and growth patterns are consistent with an assignment to $Mo(CO)_4$ and $Mo(CO)_3$. This assignment is proved by detailed ^{13}CO substitution studies which show that the $Mo(CO)_4$ adopts a C_{2v} structure (angles 174°, 107°) and the $Mo(CO)_3$ a C_{3v} structure (angle 105°). The spectra of $Mo(CO)_4$ and $Mo(CO)_3$ in CH_4 are sufficiently similar to the spectra in Ar and to the spectra of the Cr and W systems for a preliminary assignment of the bands of these systems to be made. The origin of these asymmetric structures is discussed in relation to recent theories of bonding in carbonyl fragments.

The first three papers[1-3] in this series discussed the structure and properties of $M(CO)_5$ (M = Cr, Mo, W), the primary photolysis products of the metal hexacarbonyls in a matrix. The C_{4v} structure of $M(CO)_5$ in CH_4 and Ar matrices was demonstrated using isotopic substitution.[2] While long-wavelength irradiation of $M(CO)_5$ caused the regeneration of $M(CO)_6$, on prolonged uv photolysis further bands appeared.[1,4] In this paper, it is shown that these secondary photolysis products are low-symmetry carbonyls containing fewer than five CO groups.

Experimental Section

All experiments were performed at 20°K on an Air Products Displex CS202 refrigerator equipped with an automatic temperature controller. The detailed equipment has been described elsewhere.[1,5] Matrices were deposited by the pulsed technique with concentrations of 1:3000. Ir spectra were taken on a modified Grubb Parsons Spectromajor using the second order of the lower grating giving 0.6 cm^{-1} resolution. Spectra were calibrated with DCl and DBr and are accurate to ± 0.3 cm^{-1}. Uv-visible spectra were taken on a Perkin-Elmer 356 (see ref 5). The photolysis lamp, a Phillips HPK 125W medium pressure Hg arc, was used in conjunction with a water filter to remove heat. Visible radiation was removed with a $CoSO_4$-$NiSO_4$ filter[6] and uv radiation with a Pyrex filter ($\lambda > 285$ nm) or a Calflex C filter ($\lambda > 375$ nm). All ir spectra were taken with a Ge filter to remove the visible radiation of the Nernst glower. Isotopic samples were prepared by the gas-phase photolysis method.[2,7] The matrix gases were obtained from BOC (Grade X). The calculations were performed using the methods of refinement described for the $M(CO)_6$ and $M(CO)_5$ species.[2]

Results

Even after many hours of irradiation with the unfiltered Hg lamp, the bands of the secondary photolysis products of $Mo(CO)_6$ in an argon matrix were weak in comparison to those of $Mo(CO)_5$. However, photolysis of $Mo(CO)_6$ in a methane matrix yielded $Mo(CO)_5$ very much more rapidly than in argon; on further uv photolysis new bands grew in similar positions to those observed for Ar, but in much higher yield. Within a few minutes these bands became the strongest in the spectrum and further weaker bands were detected (Figure 1).

Irradiation with long-wavelength light ($\lambda > 375$ nm) caused reconversion of the secondary photolysis products to $Mo(CO)_5$ and $Mo(CO)_6$. By following the growth and decay of optical density of each band, those bands belonging to the same system were identified. Optical density plots for all the observed bands show that the ir and uv-visible bands form three groups (A-C) in addition to $Mo(CO)_6$, $Mo(CO)_5$, and CO (Figure 2, Table I). The plots also show that on progressive uv photolysis, groups A and B reach a maximum in succession. The band at 1911 cm^{-1} (C) was never observed in high yield. Like the weak high-frequency band of $Mo(CO)_5$, the high-frequency bands of A and B must be A_1 modes and can reasonably be compared. The decrease in frequency in the order $Mo(CO)_5 > A > B$ ($Mo(CO)_5$, 2093; A, 2057; B, 1981 cm^{-1}) is precisely that expected for decreasing numbers of CO groups. With the removal of each CO group, the π back-bonding to the remainder increases, causing a decrease in the frequency (cf. the nickel carbonyls[8] except that ν(CO), 4 > 3 > 1 > 2, the amonotonic order apparently being related to the absence of an $f_{CO\text{-}CO}$ term in the monocarbonyl).

Species A has four quite separate bands in the C-O stretching region (Figure 1), indicating that it contains a minimum of four CO groups. B has a high-frequency band and a closely spaced doublet at low frequency which may be split by a "matrix effect" (see below). The manner in which