Metal Carbonyl Photochemistry. Part 1. Photolysis of the Group 6 Hexacarbonyls in Hydrocarbon Glasses; the Species $M(CO)_5$, $M(CO)_4$, $M(CO)_3$, and $[M(CO)_5(OH_2)]$

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Photolysis of the Group 6 metal hexacarbonyls in hydrocarbon glasses at 80 K gives rise to species $M(CO)_n$ (n = 3—5), presumably weakly solvated, by successive CO loss. Primary and subsequent processes both show photoreversal. Slow warming leads to recombination, hexacarbonyl precipitation, poorly defined, possibly polymeric species, and formation of species $[M(CO)_5(OH_2)]$. Visible-u.v. and i.r. spectra are presented. Solute–cosolute interactions are shown to exist in H_2-doped glasses. The species $[Cr(CO)_5(OH_2)]$ is photolabile in solution but not in the glass; the implications of this are discussed.

THE photochemistry of metal carbonyls in hydrocarbon solution has been the subject of synthetic and kinetic studies,[1] and the characterisation by i.r. of photolytic fragments in glassy hydrocarbon matrices was first reported by Sheline and co-workers [2] over 15 years ago. More recently, such photolytic fragments have been fully characterised, and their interactions with matrix materials investigated, by Turner and co-workers [3-7] using matrix-deposition techniques at $\leqslant$20 K. Our own results extend and in part correct those of Sheline, and go some way towards bridging the gap between low-temperature condensed gases and the room-temperature mobile phases in which most preparative chemistry takes place. Preliminary accounts of parts of this work have already appeared.[8-10]

EXPERIMENTAL

Rigid glasses were obtained by cooling solutions of the hexacarbonyls ($\leqslant 10^{-2}$ mol dm^{-3}, *i.e.* effective matrix ratio M:C : $\leqslant$ 1 : 5 000) in carefully purified solvents using low-temperature cells. Unless otherwise stated, the solvent used was methylcyclohexane–isopentane † (4 : 1 v/v), the coolant was liquid nitrogen, and the nominal (cell-block) temperature was 78—80 K. Infrared and u.v. spectra were taken before and after cooling, and the sample was then photolysed while cold for timed intervals using a Hanovia 100-W medium-pressure Hg discharge lamp with quartz thimble, with or without filters. Changes on irradiation were monitored spectroscopically, as were subsequent changes on warming and standing. Each substance was examined several times under slightly different conditions.

Materials and Solvents.—The compounds $[Cr(CO)_6]$, $[Mo(CO)_6]$, and $[W(CO)_6]$ were obtained commercially. In some cases they were sublimed shortly before use but this made no detectable difference to their photochemistry. Methylcyclohexane and isopentane were stirred over concentrated H_2SO_4 for several days, then washed with water, aqueous sodium carbonate, and again water, dried over $Mg[SO_4]$, passed down a silica gel column to remove alkenes, and stored over $Mg[SO_4]$. When a particularly dry solvent was required, it was distilled from fresh sodium wire in a vacuum line. There is no evidence for interference by residual impurities either before or (except for one impurity, water) after matrix softening.

Cell Materials and Construction.—Most experiments were carried out in Beckman-RIIC VLT-2 variable-temperature cell holders fitted with FH-01 i.r. cells with polytetrafluoroethylene (ptfe) spacer and front gasket and lead rear gaskets to relieve strain on tightening. The cell-block temperature was monitored using a calibrated chromel–alumel thermocouple. The outer windows were of calcium fluoride, and the inner windows were in most cases of synthetic sapphire. This material was chosen, despite cost, because of its excellent u.v. and acceptable i.r. transmittance, rigidity, inertness to condensed water, thermal conductivity, and resistance to thermal shock. These windows (unlike inner windows of NaCl, KBr, or CaF_2) never cracked on thermal shock, although careful even tightening during cell assembly was essential. A disadvantage of this system was that the windows adsorbed i.r. of frequency less than 1 700 cm^{-1} and were completely opaque below *ca.* 1 200 cm^{-1}. Despite continuous pumping, some condensation of ice on the inner windows often occurred. Cooling time to 80 K from room temperature with liquid-nitrogen refrigerant was less than 10 min.

Photolysis Conditions.—Photolysis was carried out inside the assembled i.r. cell at a distance of *ca.* 10 cm from the lamp within an aluminium box equipped with a shutter to time runs. In some experiments low-energy band-pass filters (Chance-Pilkington or H.V. Skan Ltd.) were used. These were fixed to the front outer window of the VLT-2 cell, the rear outer window being blocked off to exclude unfiltered reflected light. Lamp intensity was never measured quantitatively but lamp efficiency was crudely monitored by the photolysis rate of $[Mo(CO)_6]$.

Spectra.—Spectra were in general obtained using sample and reference cells at the same temperature, since otherwise the changes in the forms even of weak solvent bands on cooling made detection of weak peaks difficult. Baselines were recorded for each solvent system whenever cells were reassembled, and periodically during use. Photolysis was routinely monitored using Perkin-Elmer 257, 457, or 577 spectrometers, while definitive spectra were obtained on a Perkin-Elmer 225 spectrometer, and individually calibrated using CO gas and/or the atmospheric water-vapour bands at 1 942.6 and 1 918 cm^{-1}.[11] Ultraviolet spectra were obtained on a Pye-Unicam SP 700 spectrometer modified to accept the VLT-2 cell.

RESULTS AND DISCUSSION

(*i*) *Photolysis.*—The spectra of the parent hexacarbonyls become sharper on cooling and shift some 3 cm^{-1} to lower frequency. The low-frequency ^{13}CO

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† 2-Methylbutane.

satellite becomes more clearly resolved, while a further weak band around 2 010 cm^{-1} in the spectrum of [Mo(CO)$_6$] can also be assigned to [Mo(CO)$_5$(^{13}CO)] by comparison with its known[12] solution spectrum. Unlike what is found in matrices deposited from the vapour,[3] there is little sign of splitting of bands, either for the parent hexacarbonyls or for the fragments discussed below. However, at concentrations above 10^{-2} mol dm^{-3} broader more complex spectra were observed due, presumably, to aggregation or even crystallisation of the hexacarbonyls. Such aggregation sometimes occurred on cooling even at lower concentrations, and could be induced by gradual warming. We infer that the glasses used were supersaturated, but contained in the main isolated solute molecules in a range of poorly differentiated sites.

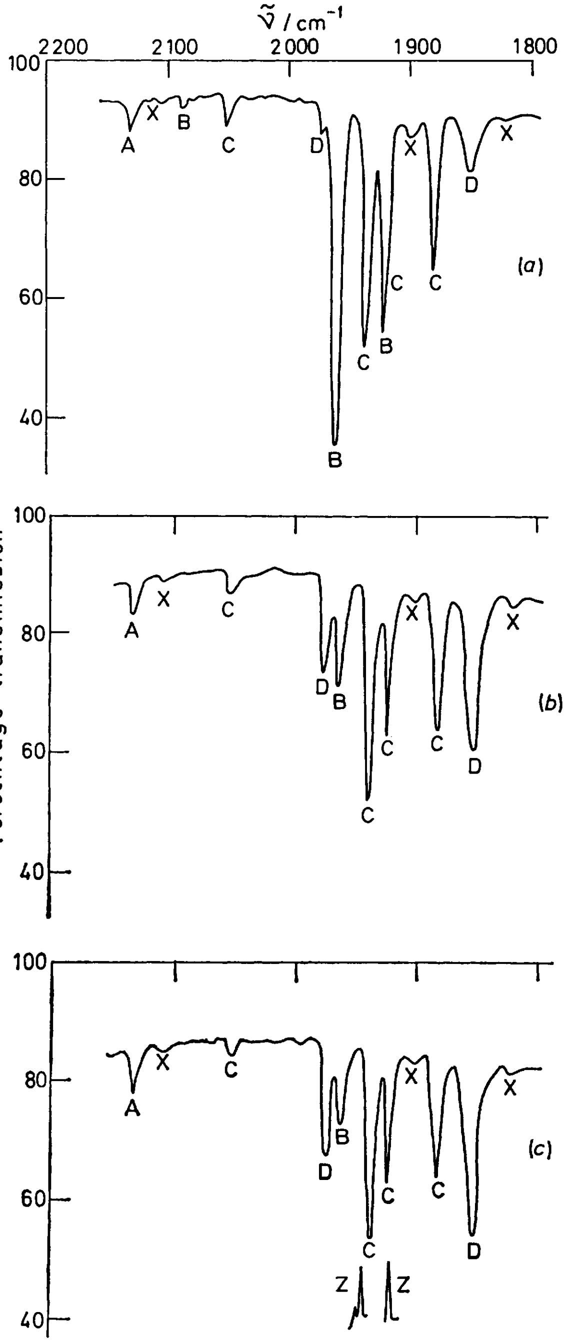

FIGURE 1 Some successive stages in the photolysis of [Mo(CO)$_6$] in hydrocarbon glass at 77 K (medium-pressure Hg lamp): (*a*) 35 min with WG 305 filter + 12 min unfiltered; (*b*) as (*a*) but another 30 min unfiltered; and (*c*) as (*b*) but another 15 min unfiltered. Assignment: A = CO, B = Mo(CO)$_5$, C = Mo(CO)$_4$, D = Mo(CO)$_3$, X = baseline error (?), and Z = atmospheric H$_2$O calibrant. Pathlength 0.1 mm; solvent methylcyclohexane–isopentane (4 : 1); 77 K; similar reference cell

Photolysis with near-u.v. light (filter WG 305; long-wavelength band pass, 305 nm cut-off) gave species with the expected three-band i.r. pattern of C_{4v} metal pentacarbonyls (weakly interacting, no doubt, with the matrix material), with occasional evidence of the ' forbidden ' B_2 mode. Further photolysis with unfiltered light led (Figure 1) to successive formation of at least two new species, assigned as M(CO)$_4$ and M(CO)$_3$ respectively (from their order of appearance, their i.r. band-intensity patterns, and their clear correlation with known matrix-isolated species[6]) with some evidence for non-linear W(CO)$_2$. Visible–u.v. spectra for the pentacarbonyls, with assignments using our general scheme,[13] are included in Table 1; unfortunately, the lower carbonyls could only be obtained as mixtures and their electronic spectra were not separated. All the pentacarbonyls showed the expected low-energy $e(xz,yz)\rightarrow a_1$ transition, while the strongest M→CO π^* charge-transfer band was shifted to lower frequency by some 3 000 cm^{-1} relative to the parent hexacarbonyls.

TABLE 1

Spectra of species M(CO)$_n$ in methylcyclohexane–isopentane (4 : 1) glasses at 77 K (this work) [a]

		Bands (cm^{-1}) [b]		
Species	Assignment	Cr	Mo	W
M(CO)$_5$	A_1	2 087	2 090	2 082
	B_2	*c*	1 997 [d]	*c*
	E	1 953	1 961	1 951
	A_1	1 925	1 922	1 921
	$d\rightarrow a_1$ [e]	19 950 (4 000)	24 200 (4 200)	23 400 (5 500) [f]
	Strongest [e] metal-ligand charge transfer	40 400 (34 000)	40 000 (45 000)	40 300 (60 000) [f]
M(CO)$_4$	A_1	2 055	2 052	2 056
	B_1	1 942	1 937	1 936
	A_1	1 920 [g]	1 921	1 917
	B_2	1 891	1 881	1 887 1 880 [h]
M(CO)$_3$	A_1	1 975	1 972	1 967
	E	1 858	1 850	1 847
M(CO)$_2$ (?)	A_1			1 909
	B_1			1 821

[a] For related spectra in methane, compare ref. 6. [b] Other weak, irreproducible, bands may be due to polymers or to impurities. [c] Not observed. [d] Possibly due to polymer. [e] Absorption coefficients (dm^3 mol^{-1} cm^{-1}) are given in parentheses. [f] Lower limit; some [W(CO)$_6$] still present. [g] Overlaps the band of Cr(CO)$_6$ at 1 925 cm^{-1}. [h] Doublet. Relative intensity changes on prolonged irradiation.

(*ii*) *Photoreversal.*—As found by Turner and co-workers [3] at lower temperatures, irradiation with light of wavelength greater than 335 nm caused reversal of photolysis; we found this for primary, secondary, and (at least for Mo) tertiary processes. Photoreversal of $Cr(CO)_4$ to $Cr(CO)_5$ was particularly ready, and perhaps for this reason $Cr(CO)_4$ was only observed as a minor product and only in the presence of $Cr(CO)_3$.

TABLE 2

Spectra (cm^{-1}) of species assigned as $[M(CO)_5(OH_2)]$

Solvent	Assignment	$[Cr(CO)_5(OH_2)]$	$[Mo(CO)_5(OH_2)]$	$[W(CO)_5(OH_2)]$
b, below 120 K	A_1		2 060	*a*
	E		1 940	1 935
	A_1		1 900	1 900sh
	$d \rightarrow a_1$ [c]	23 000	24 800	24 000
b, above 150 K	A_1	2 080	2 080	2 075
	B_2	1 975	1 980	1 984
	E	1 936	1 945	1 938
	A_1	1 908	1 910	1 906
n-Heptane, 193 K	A_1	*a*		
	E	1 935		
	A_1	1 906		
CH_2Cl_2, 193 K	A_1	*a*		
	E	1 934		
	A_1	1 890		
Wet $CF_2ClCFCl_2$, 230 K	A_1	*a*		
	E	1 935		
	A_1	1 900		

[a] Not observed. [b] Methylcyclohexane–isopentane (4 : 1). [c] Absorption coefficients not available as formation of the species was not quantitative.

(*iii*) *Reactions on Warming: Recombination.*—It is fairly easy in a sealed cell to follow the fates of photolytic fragments on matrix softening. These proved more complicated than we had expected. Between 80 and 90 K there is a change in the solvent baseline which we associate with lattice softening. This is accompanied by incomplete reversal of the initial photolyses, with disappearance of all $M(CO)_3$ and $M(CO)_4$, and some $M(CO)_5$. We suggest that if CO is close enough to some $M(CO)_n$ in the matrix, recombination can occur at this stage. Otherwise, however, different processes supervene.

(*iv*) *Formation of* $[M(CO)_5(OH_2)]$ *on Warm-up.*—At around 113 K a new species is formed, which disappears on warming to 230 K but is stable for several hours at 195 K. Prolonged initial irradiation increased the yield of the new species, as did incomplete drying of the solvent (deliberate wetting of the solvent led to precipitation of ice on cooling). The new species shows the characteristic $[M(CO)_5L]$ i.r. pattern, with the highest band being very weak, as seems usual for non-π-bonding L.* Apparently, similar species can be prepared by irradiating any of the hexacarbonyls in a sealed cell at 195 K in a variety of solvents [methylcyclohexane–isopentane (4 : 1), n-heptane, distilled dichloromethane, or $CF_2ClCFCl_2$]. The yield of the new species in dichloromethane was reduced when the solvent had been more rigorously dried (refluxing over CaH_2).

The i.r. frequencies (Table 2) of the new species are slightly higher than for $[M(CO)_5$ (alcohol)] [14,18] or $[M(CO)_5$(ether)] [8,14,18] and the electronic spectra (Table 2) are closely related to these for $M(CO)_5$ itself and $[M(CO)_5$(amine)].[3,5,19] The appearance of the spectra is highly temperature- and concentration-dependent, band broadening occurring reversibly on cooling from 175 to 115 K (see Figure 2), and sharper spectra at all temperatures being given by more dilute solutions.

The new species are not abnormal carbonyl or dinitrogen complexes, since $[Mo(CO)_5(N_2)]$ is known [20] to have a different spectrum. They are not CO_2 complexes: incorporation of dry CO_2 into the lattice does not accelerate their formation. They are not dioxygen complexes: photolysis of $[Cr(CO)_6]$ in oxygenated heptane at 195 K leads to complete disappearance of the carbonyl. They are not likely to be carboxylic acid complexes, in view of their formation in a wide range of carefully purified solvents. They are spectroscopically rather similar to, but not identical with, species $[M(CO)_5$(silicone grease)] which we deliberately prepared.

We therefore assign the new species as water complexes $[M(CO)_5(OH_2)_n]$. This accounts for their ready formation under a wide range of conditions, since water is notoriously difficult to remove completely and could be adsorbed on the steel and alumina surfaces of the cell. The water should be available for hydrogen bonding, and the observed temperature- and concentration-dependences of the spectra are consistent with aggregation by this means. All the remaining physical properties are as expected for an oxygen-bound ligand slightly more electronegative than ethers.

Above 230 K the new species disappeared and the parent hexacarbonyls were regenerated almost quantitatively; this is not surprising, since the entire reaction

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* This striking empirical result was exemplified for us by the contrast between $[M(CO)_5L]$ (L = hydrocarbon, alcohol, or ether [14]) and L = PR_3 or $P(OR)_3$. It was not unexpected in view of the predicted [15-17] effect on intensity of the difference between axial and equatorial CO stretching parameters.

sequence had been carried out in a sealed cell. The initial formation of $[M(CO)_5(OH_2)]$ rather than $[M(CO)_6]$ must reflect a kinetic preference, similar to that demonstrated by Kelly *et al.*[21] for a variety of donors at room temperature.

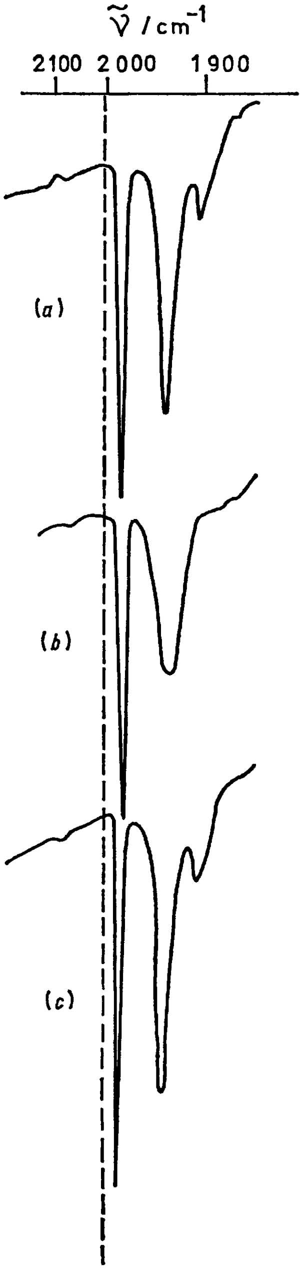

FIGURE 2 Spectrum of $[Mo(CO)_6]$ + $[Mo(CO)_5(OH_2)_n]$ in hydrocarbon solvent, obtained by warm-up of a $Mo(CO)_5$-containing glass: (*a*) at 195 K; (*b*) as (*a*), then re-frozen to 77 K; and (*c*) as (*b*), then re-warmed to 195 K

(*v*) *Other Processes*.—In many cases, the warm-up process was accompanied by cloudiness and an extremely broad, poorly reproducible, transient spectrum at around 1 950—2 000 cm^{-1}, on which peaks due to dissolved $[M(CO)_6]$ and $[M(CO)_5(OH_2)_n]$ were superposed. We tentatively assign these spectra to solid $[M(CO)_6]$, possibly in more than one crystalline modification.

In concentrated (2×10^{-2} mol dm^{-3}) solutions of $[Mo(CO)_6]$, photolysis produces bands at 2 108, 2 081vw, and 1 997 cm^{-1}. The first of these disappears on glass softening, and may be due to CO interacting weakly with some $M(CO)_n$ fragment. Such a perturbation is known for $Cr(CO)_5$ in CO-containing gas matrices from studies of the spectrum of co-ordinated CO.[7] The bands at 2 081 and 1 997 cm^{-1} grow at first on matrix softening and persist up to 113 K. These are possibly associated with a polymeric species [*e.g.* $(OC)_5MoCO \cdots Mo(CO)_5$] and may be due to the same species as is responsible for Sheline's [2] band at 1 995 cm^{-1}.* Overlap with the very weak B_2 band of $Mo(CO)_5$ itself (at 1 995 cm^{-1}) is confusing but fortuitous.

(*vi*) *Interactions in Dihydrogen-containing Glasses*.—The behaviour of $[Mo(CO)_6]$ was studied in glasses formed from solutions that had been swept with H_2. In these glasses (although not in the room-temperature solutions) the ν(CO) E_g band of $[Mo(CO)_6]$ was clearly resolved at 2 020 cm^{-1}, in good agreement with the value accepted [12] for hydrocarbon solution at room temperature.

We infer that dihydrogen can become trapped in the same solvent cavity on freezing as $[Mo(CO)_6]$, producing distortion and weakening of the glass near some (although not necessarily all) of the dissolved $[Mo(CO)_6]$ molecules. In agreement with this hypothesis, the band at 2 020 cm^{-1} disappeared completely while some $[Mo(CO)_6]$ was still present, and the B_2 band of $Mo(CO)_5$ at 1 995 cm^{-1}, with which E_g of $[Mo(CO)_6]$ is directly correlated, was unusually pronounced. Production of $[Mo(CO)_6]$ and $[Mo(CO)_5(OH_2)]$ on warming occurred unusually readily. Results in D_2-saturated solvents were similar and there was no evidence for D_2O formation.

(*vii*) *Photochemistry of* $M(CO)_5 \cdot H_2O$.—In some experiments, species $[M(CO)_5(OH_2)_n]$ were generated by warming $M(CO)_5$-containing glasses which were then re-frozen and irradiated. In such glasses, $[M(CO)_5(OH_2)_n]$ showed little further change although $[M(CO)_6]$ present was extensively photolysed. However, when $[Cr(CO)_5(OH_2)_n]$ was photochemically generated in a sealed cell in methylcyclohexane–isopentane (4 : 1) at 195 K (filter WG 335), the process could be photoreversed using visible light (filter GG 420, *i.e.* $\lambda > 420$ nm).

We suggest that $[Cr(CO)_5(OH_2)]$ tends to undergo photolysis by loss of H_2O, which is an expected process [1] for the system in the lowest excited configuration.† In a rigid glass the relatively bulky H_2O or $(H_2O)_n$ molecule cannot escape and is recaptured. In mobile solution, under WG 335 irradiation, both $[Cr(CO)_6]$ and $[Cr(CO)_5(OH_2)_n]$ give transient $Cr(CO)_5$, which can then combine with either CO or H_2O, so that a steady state is set up. Under GG 420 irradiation, to which $[Cr(CO)_6]$ is inert,

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* For many reasons, however, both we [10] and other workers [7] reject Sheline's suggestion that this band could be due to a trigonal-bipyramidal isomer.

† The implied breach of Adamson's rules [22] is not surprising in view of the existence of some M–C (axial) π bonding even in the first excited state.

only $[Cr(CO)_5(OH_2)_n]$ is photolysed, causing eventually complete regeneration of $[Cr(CO)_6]$ as observed.

We have already reported[23] a closely similar difference in behaviour between the rigid-glass and mobile-solution chemistry of $[W(CO)_4(PPr^i_3)_2]$. It follows that the rigidity of the matrix, as well as the electronic preference of the substrate, can affect the observed reaction. This is important in view of current interest[24] in the effects of small changes in ligand on the preferred path in matrix photolysis. However, Rest and co-workers[25] have shown that species $[W(CO)_5L]$ (L = pyridine or H_2S) do lose L in Ar at 10 K, and the effects of such large differences in matrix material and in temperature merit further study.

This work was supported in part by the S.R.C. We thank Dr. D. W. Milne for help in collecting electronic spectra.

[9/930 *Received*, 18*th June*, 1979]

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