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PHOTOCHEMICAL STUDIES OF $M(CO)_6$ (M = Cr, Mo, W) AT LOW TEMPERATURE IN SOLUTION. INFRARED SPECTRA OF $M(CO)_5$ (SOLVENT) (SOLVENT = METHYLCYCLOHEXANE, METHYLENE CHLORIDE) AND $W(CO)_5L$ (L = AROMATIC HYDROCARBON)

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Summary

The infrared spectra of $M(CO)_5(MCH)$ (MCH = methylcyclohexane; M = Cr, Mo, W), formed by 366 nm irradiation of $M(CO)_6$ at −78°C in rigorously purified methylcyclohexane, are reported. The previously reported spectrum of "$W(CO)_5$" at low temperature in methylcyclohexane/isopentane solution is attributed to $W(CO)_5$(impurity), where the impurity is probably an aromatic or olefinic hydrocarbon. Spectra in methylene chloride solution are also discussed. The photochemical reactions of $W(CO)_6$ with aromatic hydrocarbon ligands in methylcyclohexane solution were also studied at −78°C in a low temperature infrared cell. Irradiation (366 nm) of $W(CO)_6$ at −78°C in rigorously purified methylcyclohexane solution containing approximately 5% (v/v) toluene, benzene, mesitylene, biphenyl, or *p*-xylene initially produces the complex $W(CO)_5$(MCH). In the presence of the aromatic hydrocarbon, this complex is unstable and it decomposes in a dark reaction to give a complex which has an infrared spectrum typical for a C_{4v} $M(CO)_5X$ molecule. It is proposed that the product of the dark reaction is $W(CO)_5$(aromatic), formed by reaction of $W(CO)_5$(MCH) with the aromatic ligand in solution. The infrared spectra of the $W(CO)_5$(aromatic) complexes are different from the spectra previously reported for these complexes. It is shown that the spectra previously reported for $W(CO)_5$(aromatic) are actually attributable to $W(CO)_5$(hexane) (hexane was the solvent used in the previous study); these spectra were probably obtained before $W(CO)_5$(hexane) had time to react with the aromatic hydrocarbon.

Introduction

Although the room temperature substitution photochemistry of the Group VIB metal hexacarbonyls is well-developed and understood [1], the low temperature photochemistry of these complexes has at times been quite confusing. In the original low temperature study of the $M(CO)_6$ (M = Cr, Mo, W) complexes, Stolz, Dodson, and Sheline reported that irradiation of $W(CO)_6$ in a methylcyclohexane/isopentane glass produced a yellow intermediate [2]. The glass was allowed to "melt" and an infrared spectrum (which was taken immediately) showed bands at 2075w, 1936s and 1912ms cm^{-1}. This spectral pattern [3] and other chemical evidence led the authors to conclude that the yellow intermediate was the coordinatively unsaturated C_{4v} species $W(CO)_5$. In a second paper [4], these same authors reported the infrared spectrum of the intermediate at —180°C in a methylcyclohexane/isopentane glass [$\nu(C{\equiv}O)$ = 2092w, 1952s, and 1924m cm^{-1}]. These stretching frequencies were noted to be slightly higher in energy than those reported previously in the melted glass but there was no discussion of the reason for this energy shift. Turner demonstrated [5,6] that solution-to-glass energy shifts of CO stretching bands in metal carbonyl complexes are very small and so in order to explain the large energy shift described above he proposed that $W(CO)_5$ is complexed in the melted glass, most probably to $W(CO)_6$; he suggested that the complex giving rise to the infrared spectrum in the melted glass was $W_2(CO)_{11}$ [5]. However, later work by Braterman [7] and Turner [8] showed that "polymeric tungsten carbonyl" (probably $W_2(CO)_{11}$) has an infrared spectrum quite different from the spectrum of the melted glass. Thus, the cause of the energy shift in the infrared spectrum of $W(CO)_5$ between glass and solution remained an unsolved problem. As part of our interest in the photochemistry of organometallic complexes in low temperature solution, we investigated the photochemistry of the $M(CO)_6$ complexes at —78°C in methylcyclohexane and methylene chloride solutions. The results of this study led us to ascertain the origin of the energy shift described above. We report here those results.

A second confusing aspect concerning the low temperature photochemistry of the $M(CO)_6$ complexes is the report that UV irradiation of $W(CO)_6$ at —80°C in hexane solution containing 0.2 *M* toluene leads to the formation of $W(CO)_5$(toluene) [9]. The infrared spectrum reported for $W(CO)_5$(toluene) is essentially identical to the spectrum reported for $W(CO)_5$ at —180°C in a hydrocarbon glass [4]. It seemed likely that the complex thought to be $W(CO)_5$(toluene) was actually $W(CO)_5$. Accordingly, we reinvestigated the photochemical reactions of $W(CO)_6$ with toluene and other aromatic hydrocarbons at —78°C in methylcyclohexane solution in order to determine if complexes of the type $W(CO)_5$(aromatic) actually form. Herein we also report the results of that investigation.

Experimental

Tungsten hexacarbonyl was obtained from Strem Chem. Co. Toluene was obtained from Fisher, benzene from Amend Chem. Co. and biphenyl, *p*-xylene and mesitylene from Aldrich. Methylcyclohexane (Certified Grade) was obtained from Fisher.

All irradiations were performed with 366 nm radiation from a 200 W high pressure Hg arc. The 366 nm Hg line was isolated with a Corning CS 7-83 filter. Methylcyclohexane was used as the solvent for all of the low temperature irradiations involving reactions of $W(CO)_6$ with aromatic hydrocarbons. The photolysis solutions were about 0.002 *M* in $W(CO)_6$. The following percentages (volume/volume) of aromatic ligands in solution were used: toluene, 2%; benzene, 5%; *p*-xylene, 2%; mesitylene, 5%; biphenyl, 5%. The solutions were degassed prior to irradiation by purging with a stream of pre-purified nitrogen.

The technique for filling the IR cells under oxygen-free conditions has been previously described [10].

The photochemical reactions were monitored by infrared spectroscopy using a Perkin-Elmer 621 instrument. The spectra were calibrated against the known peaks of polystyrene. Solutions for room temperature photolysis were irradiated in conventional solution infrared cells. Low temperature infrared experiments were done with a Specac low temperature IR apparatus using a low temperature cell with NaCl windows. The cell was cooled using a Dry Ice/acetone mixture in the Dewar section of the apparatus. The "warm-up" experiments were performed by removing the cooling mixture from the Dewar and monitoring the infrared spectrum as the photolysis solution warmed to room temperature. A water filter placed between the lamp and infrared cell prevented excessive heating of the photolysis solutions during the irradiations. The dark reactions of the coordinatively unsaturated intermediates to form the impurity complexes generally occurred in one to five minutes. In order to record the infrared spectral changes accompanying the reactions, it was sometimes necessary to monitor spectral changes for the regions 2100—2050 cm^{-1} and 1960—1875 cm^{-1} in separate experiments. (Control experiments showed the absence of spectral changes outside these two spectral regions, see Table 1). The procedure was as follows: a spectrum was obtained by scanning from 2100 to 2050 cm^{-1}; the spectrophotometer wavelength was returned to 2100 cm^{-1} and the region was immediately rescanned. The spectral region was rescanned until no further spectral changes were observed. A second photolysis experiment was then performed and spectral data were obtained for the region 1960—1875 cm^{-1}. Because such a small spectral region was being scanned, there was no difficulty in obtaining successive spectra approximately one minute apart.

TABLE 1

INFRARED SPECTRAL DATA FOR THE C_{4v} $M(CO)_5X$ COMPLEXES

Complex	Solvent [a]	Temperature (°C)	$\nu(C\equiv O)$	(cm^{-1}) [b]	
"$W(CO)_5$" [c]	MCH/IP glass	—180	2092	1952	1924
"$W(CO)_5$" [d]	MCH/IP	<—78	2075	1936	1912
$W(CO)_5$(MCH)	MCH	—78	2079	1949	1922
$W(CO)_5$(impurity) [f]	MCH	—78	2074	1936	1912
$W(CO)_5$(toluene)	MCH	—78	2075	1933	1906
$W(CO)_5(CH_2Cl_2)$	CH_2Cl_2	—78	2085	1946	1903
$W(CO)_5$(impurity) [g]	CH_2Cl_2	—78	2075	1933	1879
"$Mo(CO)_5$" [c]	MCH/IP glass	—180	2093	1960	1922
$Mo(CO)_5$(MCH)	MCH	—78	[e]	1957	1920
$Mo(CO)_5$(impurity) [f]	MCH	—78	2082	1946	1913
"$Cr(CO)_5$" [c]	MCH/IP glass	—180	2088	1955	1928
$Cr(CO)_5$(MCH)	MCH	—78	[e]	1953	1927
$Cr(CO)_5$(impurity) [f]	MCH	—78	2073	1940	1908

[a] MCH = methylcyclohexane, IP = isopentane. [b] The high energy band is weak, the middle band is strong, and the low energy band is medium in intensity. [c] See ref. 4. [d] See ref. 2. [e] This band was too weak to be observed. [f] The impurity here is the impurity in MCH solvent. [g] The impurity here is the impurity in CH_2Cl_2 solvent.

TABLE 2

CARBONYL STRETCHING FREQUENCIES OF THE $W(CO)_5$(AROMATIC) COMPLEXES AT −78°C IN METHYLCYCLOHEXANE [a]

Complex	$\nu(C\equiv O)$ (cm^{-1})	ref.
$W(CO)_6$	1983s	This work; 11
$W(CO)_5$(MCH)	2079, 1949, 1922	This work
$W(CO)_5$(toluene)	2075, 1932, 1909	This work
$W(CO)_5$(toluene)	2083, 1947, 1921	9
$W(CO)_5$(benzene)	2072, 1930, 1906	This work
$W(CO)_5$(benzene)	2083, 1948, 1921	9
$W(CO)_5$(biphenyl)	[b], 1931, 1908	This work
$W(CO)_5$(biphenyl)	2083, 1949, 1922	9
$W(CO)_5$(*p*-xylene)	2070, 1935, 1912	This work
$W(CO)_5$(*p*-xylene)	2082, 1945, 1920	9
$W(CO)_5$(mesitylene)	2077, 1942, 1915	This work
$W(CO)_5$(mesitylene)	2082, 1943, 1915	9

[a] Where not given, the following intensities apply: the high energy band is weak, the middle energy band is strong, and the low energy band is medium in intensity. [b] This band was too weak to be observed.

Isolation of the $W(CO)_5$(aromatic) complexes was attempted but was unsuccessful because the complexes are stable only at low temperature. When solutions of $W(CO)_5$(aromatic) in the low temperature IR cell were warmed to room temperature, the complexes backreacted with the CO in the sealed cell and $W(CO)_6$ was reformed. The backreaction was spectroscopically observed by monitoring the warm-up using infrared spectroscopy; the $W(CO)_6$ band at 1983 cm^{-1} [11] increased in intensity and the $W(CO)_5$(aromatic) bands (Table 2) decreased in intensity. In an attempt to prevent the backreaction of $W(CO)_5$-(aromatic) with CO, the photolysis solution was purged with nitrogen. Thus, $W(CO)_6$ in methylcyclohexane containing 5% toluene was irradiated (366 nm) at −78°C in a septum-stoppered quartz cell. The solution was purged by a stream of nitrogen gas introduced by a needle. After 15 minutes of irradiation, the solution was warmed to room temperature while still maintaining the nitrogen purge. The infrared spectrum of the room temperature solution showed no bands attributable to $W(CO)_5$(toluene). In a final attempt to isolate a substitution product, $W(CO)_6$ was irradiated (366 nm) in neat benzene and toluene at room temperature. No isolable products were formed.

Results and discussion

Tungsten hexacarbonyl in methylcyclohexane at −78°C was irradiated at 366 nm in a low temperature infrared cell. The reaction was monitored by infrared spectroscopy. Successive infrared spectra clearly showed the disappearance of the $W(CO)_6$ band [11] at 1983 cm^{-1} and the appearance of bands at 2079w, 1949s, and 1922m cm^{-1}. These latter bands were present only momentarily because the complex giving rise to them decomposed in the dark in several minutes to a complex with bands at 2074w, 1936s, and 1912m cm^{-1}. In other words, irradiation of $W(CO)_6$ at −78°C initially produces the species observed by Stolz, Dodson, and Sheline in a glass [4], and then this species is transformed to the complex observed by these same authors in the melted glass

[2]. This latter complex is apparently stable indefinitely at —78°C but when the solution is warmed to room temperature the bands at 2074, 1936, and 1912 cm^{-1} disappear and the band at 1983 cm^{-1} reappears, i.e. $W(CO)_6$ is regenerated [12]. Similar infrared spectral changes were observed at —78°C for $Cr(CO)_6$ and $Mo(CO)_6$ in methylcyclohexane (Table 1).

The infrared spectra of the "low energy" and "high energy" forms (as they will henceforth be called) of the low temperature intermediate are both typical of a C_{4v} $M(CO)_5$ or $M(CO)_5X$ species [3]. Thus, it seems unlikely that a geometrical isomerization is occurring in the transformation of the high energy to the low energy species. A logical explanation is that the $M(CO)_5$(solvent) [13] species initially produced by the irradiation is reacting with an impurity in the solvent to form $M(CO)_5$(impurity). In order to verify this hypothesis, the methylcyclohexane solvent was carefully purified by standard procedures [14—16]. However, when the experiments described above were repeated with the purified solvent there was no change in any of the spectral features noted above. This result does not necessarily invalidate the hypothesis because Murray and Keller have noted that hydrocarbon solvents purified by standard procedures still contain small amounts of impurities [18]. Accordingly, they developed a purification procedure which gives hydrocarbon solvents of the utmost purity [18]. Using methylcyclohexane purified by their method, the photochemical reactions described above were again repeated. In this case, only the bands attributable to the high energy form of the intermediate were observed in the infrared spectrum; there was no decomposition of this high energy species to the low energy species. The photochemical reactions in the highly-purified methylcyclohexane were reversible at —78°C; the $M(CO)_6$ complex was totally regenerated in about one hour under the conditions used in our experiments [11]. From these observations we conclude that the high energy form of the C_{4v} intermediate is $M(CO)_5$(methylcyclohexane) and that the low energy form (i.e. the C_{4v} intermediate originally observed by Stolz, Dodson, and Sheline [2] in the melted glass), is $M(CO)_5$(impurity). Aromatic and olefinic hydrocarbons are the major impurity in methylcyclohexane [18] so the "impurity" complex is probably $M(CO)_5(\eta^2$-aromatic) or $M(CO)_5$(olefin).

Unfortunately, the purification of methylene chloride using standard methods [15,16] was apparently not rigorous enough. Irradiation of $M(CO)_6$ at —78°C in "purified" methylene chloride produced a high energy form of the intermediate which decomposed to a low energy species (Table 1). However, we believe that the low energy species in methylene chloride is also $M(CO)_5$(impurity). The following observation supports this belief. In purified methylene chloride, the high energy intermediate still decomposed to the low energy species, however, after a small amount of the low energy complex had appeared, continued irradiation produced only the high energy intermediate — further decomposition to the low energy species did not occur. Apparently, after purification only traces of impurity are in the solvent and this is used to form $M(CO)_5$(impurity). When all of the impurity has reacted with $M(CO)_5(CH_2Cl_2)$ [13] to form $M(CO)_5$(impurity) then any more $M(CO)_5(CH_2Cl_2)$ that is generated is stable.

Irradiation (366 nm) of $W(CO)_6$ at —78°C in methylcyclohexane solution containing 2% (v/v) toluene causes the following infrared spectral changes to

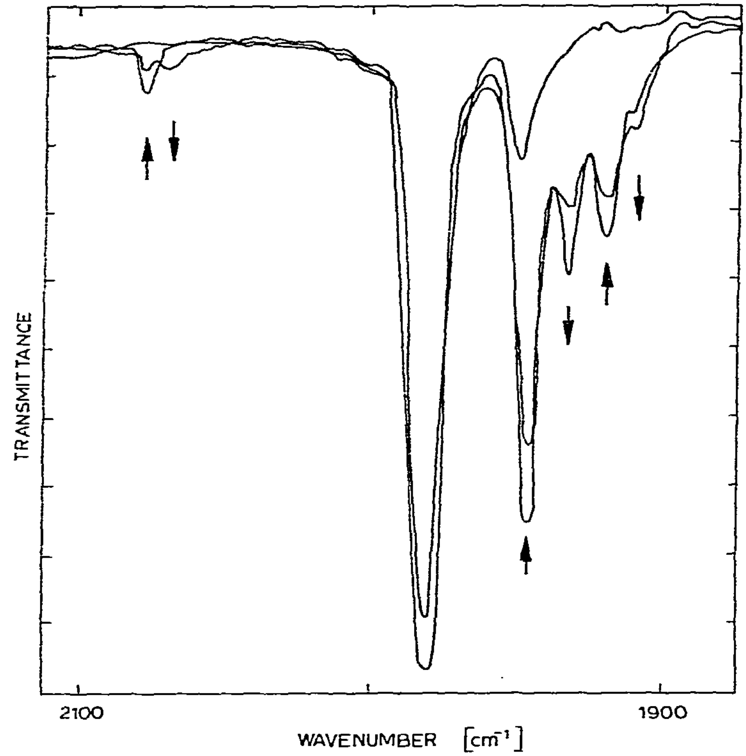

Fig. 1. Infrared spectral changes resulting from 366 nm irradiation at —78°C of $W(CO)_6$ in purified methylcyclohexane containing 2% toluene. The arrows show the direction of changes for the conversion of $W(CO)_5$(MCH) to $W(CO)_5$(toluene). The intense band at 1983 cm^{-1} is $W(CO)_6$. Similar spectral changes are observed using unpurified methylcyclohexane.

occur: the intense $W(CO)_6$ band at 1983 cm^{-1} [11] decreases in intensity and six new bands appear at 2079, 2075, 1949, 1932, 1922 and 1909 cm^{-1} (Fig. 1). Further spectral changes occur without irradiation when the solution is kept at —78°C: the bands at 2079, 1949, and 1922 cm^{-1} decrease in intensity and the bands at 2075, 1932, and 1909 cm^{-1} increase in intensity. The complex $W(CO)_5$(MCH) has bands in the CO stretching region at 2079w, 1949s, and 1922m cm^{-1}. A comparison of this data to the data above reveals that the complex which appears upon irradiation and then disappears in the dark reaction is $W(CO)_5$(MCH). Control experiments showed that $W(CO)_5$(MCH) is the only product formed when $W(CO)_6$ is irradiated at —78°C in purified methylcyclohexane without added toluene; there was no dark reaction to form another tungsten carbonyl species. It is logical to conclude, therefore, that the dark reaction involves the reaction of $W(CO)_5$(MCH) with the added toluene to form $W(CO)_5$(toluene). The overall reaction scheme is shown below.

$$W(CO)_6 \xrightarrow[\text{MCH solvent}]{\text{366 nm, }-78^\circ\text{C}} W(CO)_5(\text{MCH}) \xrightarrow[\text{(dark reaction)}]{\text{toluene, }-78^\circ\text{C}} W(CO)_5(\text{toluene})$$

The infrared spectrum of the final product (2075w, 1932s, 1909m cm^{-1}) is typical for a C_{4v} $M(CO)_5X$ complex [3] and is consistent with the formulation $W(CO)_5$(toluene). The only likely alternative to $W(CO)_5$(toluene) for the dark reaction product would be $W_2(CO)_{11}$, formed by reaction of $W(CO)_5$(MCH) with $W(CO)_6$. Two points argue against this interpretation. First, Braterman [7] and Turner [8] have shown that "polymeric tungsten carbonyl" (probably $W_2(CO)_{11}$) has an infrared spectrum very different from the spectrum of the product formed in the dark reaction. Second, the dark reaction occurs only when toluene is present in solution; it is difficult to see why $W_2(CO)_{11}$ would not form in pure methylcyclohexane.

The infrared spectrum of $W(CO)_5$(toluene) has been previously reported [9]; the complex was generated photochemically at −80°C in hexane solution containing 0.2 *M* toluene and it was reported to have CO stretching bands at 2083w, 1947s, and 1921m cm^{-1}. Based upon our results we suggest that these bands are actually attributable to $W(CO)_5$(hexane) [19]. In methylcyclohexane solution containing 2% (v/v) toluene the reaction of $W(CO)_5$(MCH) with toluene is reasonably slow at −78°C (it takes about ten minutes for all the $W(CO)_5$(MCH) to disappear) [20] so the previously reported spectrum was probably obtained before sufficient $W(CO)_5$(toluene) had formed in the dark reaction. Note that the previously reported [9] spectrum of $W(CO)_5$(toluene) was obtained in a 0.2 *M* solution of toluene in hexane. This corresponds to about a 2% (v/v) solution of toluene in hexane which is very similar to the concentration of toluene used in our experiments. Therefore, it is reasonable that the previous investigators [9] observed $W(CO)_5$(hexane) in the infrared spectrum and that it was necessary to wait for the dark reaction before $W(CO)_5$-(toluene) could be observed.

Results similar to those described above for toluene are also obtained when $W(CO)_6$ is irradiated at −78°C in methylcyclohexane containing 5% benzene, 2% *p*-xylene, 5% mesitylene, or 5% biphenyl. In each case, $W(CO)_5$(MCH) was observed to form initially upon irradiation. This complex then reacted in a dark reaction and a new set of infrared bands grew in intensity. These latter bands are once again assigned to the complexes $W(CO)_5$(aromatic). The $\nu(C\equiv O)$ data for the complexes are listed in Table 2. With the exception of $W(CO)_5$(mesitylene), the infrared spectral data for $W(CO)_5$(aromatic) in Table 2 are different from the $\nu(C\equiv O)$ values previously reported for these complexes [9]. In the cases where a difference exists, the previously reported spectrum of $W(CO)_5$-(aromatic) can be assigned to $W(CO)_5$(hexane).

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12 The backreaction of the low temperature intermediate with CO is possible because the low temperature infrared cell is gas tight. Hence, the CO generated by the irradiation of $M(CO)_6$ is still present in the cell.

13 It is now generally recognized that the vacant coordination site of a coordinatively unsaturated complex is occupied by a solvent molecule [6].

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19 There should be very little difference in the interactions between $W(CO)_5$ with hexane and methylcyclohexane; consequently the infrared spectra of $W(CO)_5$(MCH) and $W(CO)_5$(hexane) should be nearly identical.

20 In solutions containing a large excess of toluene, the formation of $W(CO)_5$(toluene) is very rapid. For example, when $W(CO)_6$ is irradiated at −78°C in methylcyclohexane solution containing 10% (v/v) toluene, the only product observed in the infrared spectrum of the low temperature solution is $W(CO)_5$(toluene); the intermediate formation of $W(CO)_5$(MCH) was not observed.