Inorganica Chimica Acta, 29 (1978) 243–248

Photochemistry of $W(CO)_5PCl_3$ in an Ar Matrix at 10 K

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Received December 10, 1977

The infrared and UV–visible spectra of $W(CO)_5PCl_3$ *in an Ar matrix at 10 K are presented. The UV–visible photolysis of* $W(CO)_5PCl_3$ *with different wavelengths (*λ *= 229, 254, 280, 313 and 366 nm) resulted in release of phosphorus trichloride. This remarkable photochemical behaviour of* $W(CO)_5PCl_3$*, different from W(CO)*$_5$*(amine) is discussed in terms of a m.o. scheme. The complete infrared and UV–visible spectra of* $W(CO)_5PCl_3$ *in different media are assigned.*

Introduction

In the last few years several papers have been published about the photochemistry in low temperature matrices of Group VI hexacarbonyls [1–5]. Recently, the photochemistry of substituted carbonyls at low temperatures has been presented [6–10]. The substituted carbonyls showed different photochemical processes depending both on the type of ligand and the irradiated wavelength:

$$M(CO)_5L \xrightarrow{h\nu} M(CO)_4L + CO$$

$$M(CO)_5L \xrightarrow{h\nu'} M(CO)_5 + L$$

Poliakoff [9, 10] reported the photochemistry of transition metal thiocarbonyl complexes in several matrices. He obtained evidence for the formation of two isomeric forms of $M(CO)_4CS$ after UV-photolysis (λ = 300 nm) of $M(CO)_5CS$ (M = Cr, or W). After long periods of irradiation with visible light, the parent compound $M(CO)_5CS$ could be reformed. Poliakoff found no evidence for the loss of CS. Black [6] obtained the same results with $Mo(CO)_5PCx_3$ (Cx = cyclohexyl) in a hydrocarbon glass. Rest [8] published the photochemistry of $W(CO)_5L$ (L = pyridine or 3-bromopyridine). Irradiation of $W(CO)_5L$ with a low-pressure Hg lamp (λ = 254 nm) resulted in the release of CO. However, photolysing with a filtered medium pressure Hg arc ($320 < \lambda < 390$ nm) resulted in the formation of $W(CO)_5$. Subsequent irradiation at 435 nm reversed the reaction.

In this paper, we report the loss of the phosphorus ligand when $W(CO)_5PCl_3$ in an Ar matrix at 10 K is irradiated with UV–visible light (λ = 229, 254, 280, 313, 366 nm). Subsequent irradiation with λ = 435 nm resulted in formation of the parent compound. The infrared and UV–visible spectra of $W(CO)_5PCl_3$ in different media (solution, gas phase and Ar matrix) are presented with a complete assignment. The differences in the photochemistry of $W(CO)_5PCl_3$ and $W(CO)_5$(amine) are discussed.

Experimental

$W(CO)_5PCl_3$ was prepared under dry deoxynated nitrogen from the corresponding $W(CO)_5THF$ complex. PCl_3 and $W(CO)_6$ were bought from respectively Merck and Strem and used without further purification. Argon with a purity of 99.999% was employed.

An Air Products Displex model CSW-202B closed cycle helium refrigerator was used with temperature readout model APD-T_1. The temperature was measured with a gold plus iron .07% atomic *vs.* chromel thermocouple. A vacuum shroud model DMX-1 AE was supported with two high purity, quartz epoxied to stainless steel windows and two CsBr windows. The sample window of CsI was fitted with two rings of indium wire. With an Edwards Diffstack pump system 100/300, supplied with a liquid nitrogen trap, a vacuum better than 10^{-6} torr could be maintained. The desired gas mixture of Ar and $W(CO)_5PCl_3$ was achieved by adding Ar to the vapour pressure of the sample. This procedure was carried out in the dark, because $W(CO)_5PCl_3$ decomposes slowly in daylight. The vapour pressure of $W(CO)_5PCl_3$ was measured with a Knudsen cell of 1 mm, as will be published elsewhere [11]. The best results were obtained when a mixture of 1:6,500 sample-to-matrix gas was used and by pulsing a volume of 20–30 ml with a pressure of 300–400 torr at the cold window.

This technique was applied for the first time by Rochkind [12] and was extensively studied by Perutz and Turner [13].

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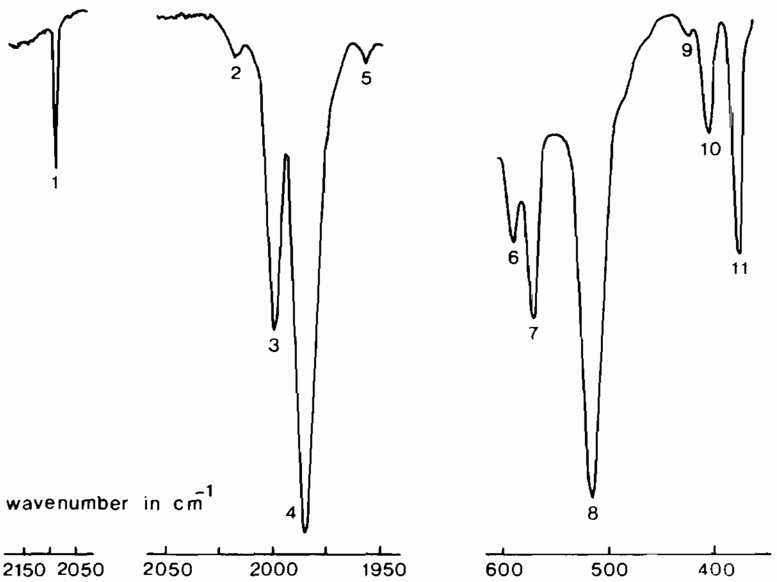

Figure 1. Ir spectrum of $W(CO)_5PCl_3$ in an Ar matrix at 10 K, after deposition (below 600 cm^{-1} the spectrum was recorded with ordinate scale expansion).

Infrared spectra were recorded both on a Beckman IR-7 and on a Beckman IR-4250 spectrometer. The spectrometers were calibrated with DCl and H_2O, using the IUPAC wavenumber tables. In order to remove UV and visible light from the Nernst glower, we used a Si filter of 2 mm thickness. UV–visible spectra were recorded on a Unicam SP 700 spectrometer with optical density screens in the reference. The spectrometer was calibrated using benzene vapour.

In order to photolyse the sample, two light sources were used: a Philips 25 W Cd-line source, model 93107 with a strong emission at 229 nm and a Philips HPK 125 W high pressure Hg lamp. The mercury lamp was filtered using interference filters, λ = 254, 280, 313, 366 nm from Meyvis and a Balzers B 40, λ = 436 nm filter. During the photolysis with the high pressure arc a quartz water cell of 5 cm was used to remove the heat as much as possible.

Results

IR Spectra

The IR spectrum of $M(CO)_5PCl_3$ (M = Cr, Mo, W) is well known, with the exception of the region below 650 cm^{-1}, when M = Cr, W [14, 15]. The $W(CO)_5PCl_3$ molecule is expected to have local C_{4v} symmetry. The three main IR bands, found in an Ar matrix at 10 K ($2a_1$ + e) confirm this structure (Table I, Figure 1). The formally infrared inactive b_1-mode appeared as a weak feature. Apparently the phosphorus ligand reduces the overall symmetry and this probably results in activation of forbidden infrared-bands, as has been demonstrated for $M(CO)_5PPh_3$ [16, 17]. The e-mode of the $W(CO)_4$-(^{13}CO)PCl_3 molecule was assigned to the band at 1954 cm^{-1}. In the low frequency region four (a_1 + 3e), δ(M–C–O) and three ($2a_1$ + e), ν(M–C) vibrations are expected. We found two δ(M–C–O) bands at 587 and 569 cm^{-1} and three ν(M–C) vibrations at 424, 404 and 377 cm^{-1} in agreement with the results of Poilblanc [14]. The ν(P–Cl) was found at 515 cm^{-1}. The ν(W–P) expected to occur below 250 cm^{-1} could not be detected in this region [17]. However, a strong band at 300 cm^{-1} was measured, which possibly could be assigned to ν(W–P).

The influence of the media (n-hexane, gas phase, Ar matrix) is demonstrated in Table I.

UV–Visible Spectra

The absorption spectra of some $W(CO)_5L$ complexes have been described in the literature [18–25]. With L = PCl_3 only the absorption spectrum of $Mo(CO)_5PCl_3$ has been published [15]. We studied the UV–visible spectrum of $W(CO)_5PCl_3$ in n-hexane at room temperature and in an Ar matrix at 10 K. The results are compiled in Table II.

The two charge transfer (d $\rightarrow$ π*CO) transitions were assigned to the 225 and 290 nm bands, just as for $W(CO)_6$ [26] and $W(CO)_5L$ [19]. The ligand field transitions were found at 351 and 374 nm ($^{1,3}E \leftarrow {}^1A_1$). The shoulder at 208 and 243 nm could be assigned to an intraligand transition (n $\rightarrow$ δ^*PCl_3) [27] and a charge transfer to PCl_3 transition, respectively. The UV–visible spectrum of $W(CO)_5PCl_3$ showed small changes on going from

TABLE I. Infrared Frequencies of M(CO)$_5$PCl$_3$ in cm^{-1}.

Assignments		Intensity	Mo(CO)$_5$PCl$_3$ hydrocarbon^a	W(CO)$_5$PCl$_3$ hydrocarbon	W(CO)$_5$PCl$_3$ gas phase	W(CO)$_5$PCl$_3$ Ar matrix at 10 K	Band No.
νC–O	A_1	w	2095	2095^a	2100.2	2098.5	1
	B_1	w	2018	2019		2020.8	2
	A_1	m	1999	1990	2006.7	2000.0	3
	E	s	1985	1984	1994.4	1986.1	4
ν^{13}C–O	E	w		1951.3^b	1962.7	1954.2	5
νM–C–O	A_1	s	589	584	586	587	6
	E	s	571	566	569	569	7
		vw	549				
		vw	526				
		vw	476				
νP–Cl	A_1	s	502	511	519	515	8
νM–C	A_1	vw	400	424		424	9
	A_1	m	382	401	400	404	10
	E	s	366	374	377	377	11

^{a}Reference 14. ^{b}Measured in n-hexane.

TABLE II. UV–visible Wavelengths of M(CO)$_5$PCl$_3$ in nm.

Assignments	Mo(CO)$_5$PCl$_3$ n-hexane^a	W(CO)$_5$PCl$_3$ n-hexane	W(CO)$_5$PCL$_3$ Ar matrix 10 K^b
n → δ*(PCl$_3$)		208	
d → π*(CO)	231	225	224
d → π*(PCl$_3$)	246	243	242
d → π*(CO)	290	290	289
d → d(S–S)	355	351	350
d → d(S–T)		374	

^{a}Reference 15. ^{b}Recorded with NaCl as a sample window.

n-hexane at room temperature to an Ar matrix at 10 K.

Photochemistry

Irradiation of W(CO)$_5$PCl$_3$ in an Ar matrix at 10 K with UV–visible light (λ = 229, 254, 280, 313, 366 nm) resulted after a few minutes in the appearance of two new infrared bands at 1963 and 1932 cm^{-1}. Below 650 cm^{-1} there were drastic changes in the spectrum. A new band at 500 cm^{-1} could be detected. Comparing these results with those obtained by Turner *et al.* [1], we can assign the 1963 and 1932 cm^{-1} bands to the e and a_1 modes of the C_{4v} W(CO)$_5$ fragment. The band at 500 cm^{-1} can be assigned to the ν_3 of free PCl$_3$, being the strongest stretching vibration of PCl$_3$ in an Ar matrix [28]. The very weak a_1 band of W(CO)$_5$, expected to occur at 2097 cm^{-1} escaped detection, probably because of the lower resolution above 2000 cm^{-1}. Prolonged photolysis with UV light resulted in the decomposition of the W(CO)$_5$ species into lower carbonyls like W(CO)$_4$ with a frequency at 1939 cm^{-1} and into free CO at 2138 cm^{-1}.

The UV–visible spectrum of W(CO)$_5$PCl$_3$in Ar at 10 K showed after photolysis loss of intensity of the parent bands. Especially the 289 nm absorption disappeared and the band at 242 nm became broader. A new band was found at 440 nm due to the formation of W(CO)$_5$. Exactly the same results were obtained with a filtered high pressure mercury lamp (λ = 254, 280, 313, 366 nm), an unfiltered high pressure mercury lamp and an unfiltered Cd lamp (λ = 229 nm), which indicated the absence of a wavelength dependence. The reaction was reversed by subsequent irradiation with λ = 436 nm, as has been found for W(CO)$_6$ and W(CO)$_5$ pyridine [1, 8] (Fig. 3).

Discussion

Hexacarbonyls of Group VI showed in matrices a distortion from O_h to D_{2h} symmetry [1]. A distortion of the local C_{4v} symmetry of W(CO)$_5$PCl$_3$ in an Ar matrix at 10 K could not be detected in the infrared which is in agreement with the observations of Poliakoff [9] in his studies of M(CO)$_5$CS molecules.

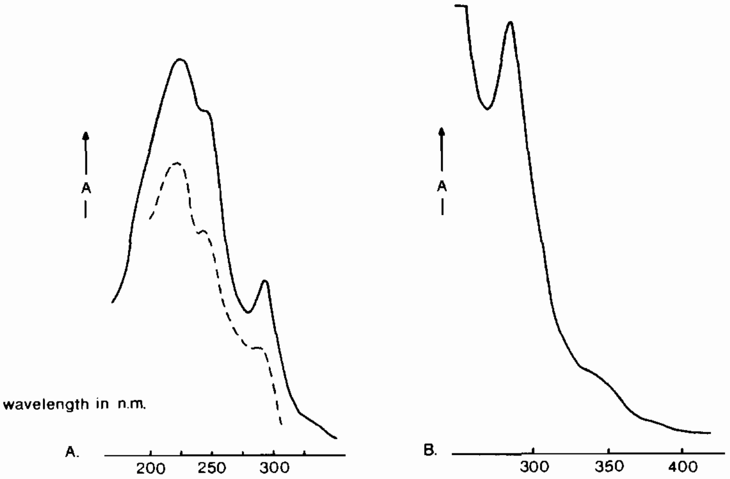

Figure 2. UV–visible absorption spectra of $W(CO)_5PCl_3$. A: (———) spectrum in n-hexane at room temperature; (- - - - -) spectrum in an Ar matrix at 10 K. B: (———) concentrated spectrum in n-hexane (in an Ar matrix only a very weak band at 350 nm was detected).

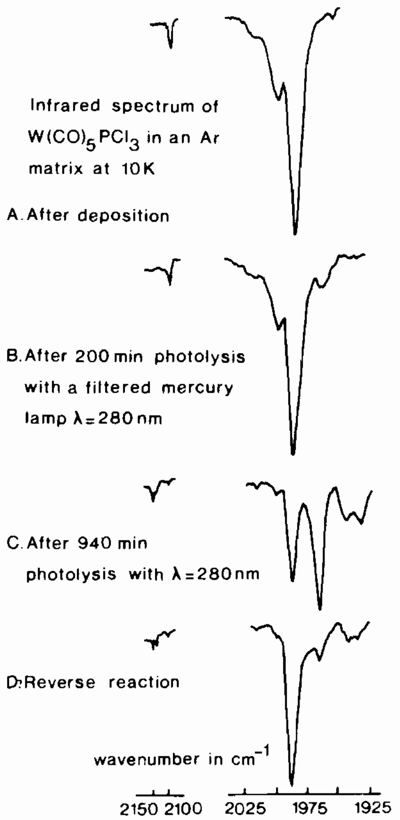

Figure 3. Infrared spectrum of $W(CO)_5PCl_3$ in an Ar matrix at 10 K. A: after deposition; B: after 200 min photolysis with a filtered mercury lamp λ = 280 nm; C: after 940 min photolysis with λ = 280 nm; D: reverse reaction.

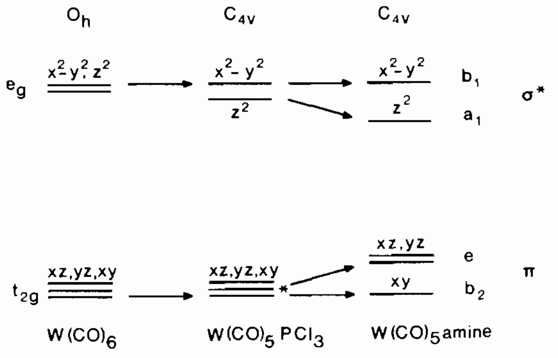

Figure 4. Diagram of the d-orbitals, showing the relative magnitudes of the splittings on going from $W(CO)_6$ to $W(CO)_5PCl_3$ and $W(CO)_5$(amine) [*]. In the photoelectron spectrum of $W(CO)_5PCl_3$ a splitting of the d_{xz}, d_{yz} and d_{xy}-orbitals was not observed [32].

The UV–visible spectrum of $W(CO)_5PCl_3$ at 10 K showed small changes compared with the UV–visible spectrum in n-hexane at room temperature, as has been found for $M(CO)_6$ [1] (Fig. 2). For several types of complexes, changes in UV, infrared and in the Raman spectra are found and are under study in our laboratory [29].

UV–visible photolysis of $W(CO)_5PCl_3$ in an Ar matrix resulted in formation of $W(CO)_5$. No evidence was found for the formation of $W(CO)_4PCl_3$. These results seem to be contrary to the results of the photolysis of $W(CO)_5$(pyridine) in an Ar matrix at 12 K [8] and the results obtained by Wrighton [18, 20] and Schwenzer [30] for the photosubstitution processes of $M(CO)_5$(amine) (M = Mo, W; L = NH_3, n-$PrNH_2$, piperidine, pyridine) and $M(CO)_5$(phosphine) (M = Cr, Mo, W; L = $P(C_6H_5)_3$, P(cyclohexyl)$_3$) respectively, both in solutions at room temperature. Wrighton found efficient loss of CO during short-wavelength irradiation (λ = 254 nm) and loss of the amine ligand by irradiation with λ = 436 nm.

These and our results can be explained by the relative magnitudes of the d-orbital splittings as is shown in Figure 4.

The relative positions of d_{z^2} and $d_{x^2-y^2}$ have been described in several conflicting papers [18, 20, 23]. We assign the lowest lying σ^* orbital to the d_{z^2}-orbital. This assignment is supported by the diagram published by Cotton [23], when the e^2/r_{ij} correction factor is taken into account [31].

In $W(CO)_5$(amine) the lowest lying ligand field transition $^{1,3}E \leftarrow {}^1A_1$ results in depopulation of the d_{xz}, d_{yz}-orbitals and population of the σ-antibonding d_{z^2}-orbital. Therefore, destabilization along the z-axis and loss of σ-bonding amine will occur during long wavelength irradiation.

Shorter wavelength photolysis will result in destabilization of M–CO π-bonding orbitals and population of the σ-antibonding $d_{x^2-y^2}$-orbital. The result is loss of CO. In the photoelectron spectrum of $W(CO)_5PCl_3$ the $e(d_{xz}, d_{yz})$ and $b_2(d_{xy})$ states coincide [32]. Thus, upon irradiation with $\lambda = 366$ nm, the lowest lying ligand field transition $^{1,3}E \leftarrow {}^1A_1$ will result in population of the σ-antibonding d_{z^2}-orbital and depopulation of the three π-bonding d_{xz}, d_{yz} or d_{xy} orbitals. Because PCl_3 is a better σ-donating ligand than CO, the photolysis with $\lambda = 366$ nm will result in loss of PCl_3.

Photolysing in higher energy ligand field excited states results in depopulation of d_{xz}, d_{yz}, d_{xy} and population of $d_{x^2-y^2}$. Loss of CO is only expected when the $^1A_2(e^4b_2\ {}^1b_1^1) \leftarrow {}^1A_1(e^4b_2^2)$ ligand field transition is irradiated. The relative positions of the d_{z^2} and $d_{x^2-y^2}$ levels in $W(CO)_5PCl_3$ are not determined. On basis of the photoelectron and UV spectra and by assuming that the $d_{x^2-y^2}$ level in $W(CO)_6$ and $W(CO)_5L$ [23] will be the same, the difference between those two levels can be estimated as small in $W(CO)_5PCl_3$. Such a small difference will cause an extremely fast non radiative decay from $^{1,3}E \leftarrow {}^{1,3}A_2$ [33] and release of PCl_3. This non radiative decay was also found in $M(CO)_5$(amine), although not so obvious [20].

This behaviour must also explain the results of the photolysis in the CT-bands of $W(CO)_5PCl_3$, with the sources $\lambda = 229, 254$ and 280 nm.

The CO substitution in $M(CO)_5L$ (M = Cr, Mo, W; L = $P(C_6H_5)_3$, P(cyclohexyl)$_3$) after UV photolysis as published by Schwenzer [30] and Black [6] can be explained in the same way as is supposed for $W(CO)_5$(amine), because of the lower π-acceptability of these ligands compared with PCl_3*. A splitting between the $e(d_{xz}, d_{yz})$ and the $b_2(d_{xy})$ states was indeed observed in the photoelectron spectra of these compounds [34], so the same explanation as for $W(CO)_5$(amine) holds.

The PCl_3 rupture was reversed with light corresponding to the visible absorption of the pentacarbonyl ($\lambda = 440$ nm). The same mechanism was found for $W(CO)_6$ [1] and $W(CO)_5$(pyridine) [8].

The results of the investigations showed definitely that even heavy ligands as PCl_3 can be generated by irradiating their carbonyl complex in an Ar matrix at 10 K.

Acknowledgements

The authors express their thanks to Mr. G. C. Schoemaker and the members of the workshop for their assistance throughout these studies. Dr. D. J. Stufkens and Drs H. Daamen are thanked for their helpful discussions.

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*The results of Black, however, can also be explained by assuming that, contrary to CO, the heavy phosphorus ligand cannot diffuse from the cage in a hydrocarbon glass at 77 K and that destabilization along the z-axis therefore leads to loss of CO.

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