Inorganica Chimica Acta, 29 (1978) L207–L209
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

The Difference in Photochemical Behaviour Between $Cr(CO)_5PCl_3$ and $Cr(CO)_5$(pyrazine) in Ar Matrices at 10 °K

GOSSE BOXHOORN and AD OSKAM*

Anorganisch Chemisch Laboratorium, J. H. van't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, Amsterdam, The Netherlands

Received April 20, 1978

The photochemistry of substituted Group VI carbonyls has been the subject of several publications [1–4]. Two photochemical reactions have been reported:

$$M(CO)_5L \xrightarrow[X]{h\nu} M(CO)_4LX + CO \qquad I$$

$$M(CO)_5L \xrightarrow[X]{h\nu'} M(CO)_5X + L \qquad II$$

X = ligand or vacancy in matrices.
The reaction path depends both on the type of ligand and on the irradiated wavelength. $M(CO)_5CS$ in a matrix [5, 6] and $Mo(CO)_5PCx_3$ (Cx = cyclohexyl) in a hydrocarbon glass follow reaction path I, forming *cis* and *trans*-$M(CO)_4LX$ species and free CO. Rest published the photochemistry of $W(CO)_5L$ (L = pyridine or 3-bromopyridine) [8]. Photolysis of $W(CO)_5L$ at 12 K in argon with $320 < \lambda < 390$ nm resulted in the formation of $W(CO)_5$. Photolysis, however, with $\lambda = 254$ nm yielded free CO and from this he concluded that both reaction I and II can occur in matrices at 12 K.

In this paper we report the difference in photochemical behaviour between $Cr(CO)_5PCl_3$ and $Cr(CO)_5$pyrazine in Ar matrices at 10 K. UV-irradiation of $Cr(CO)_5PCl_3$ yielded only $Cr(CO)_5$ and free PCl_3. In contrast, photolysis of $Cr(CO)_5$pyrazine afforded either $Cr(CO)_5$ or free CO together with a new species *cis*-$Cr(CO)_4$ pyrazine. This difference in photochemical behaviour is explained on the basis of a fast non radiative decay from the $d_{x^2-y^2}$ to the d_{z^2} orbital in the case of $Cr(CO)_5PCl_3$, although a reactive metal to ligand charge transfer state cannot be excluded.

Results and Discussion

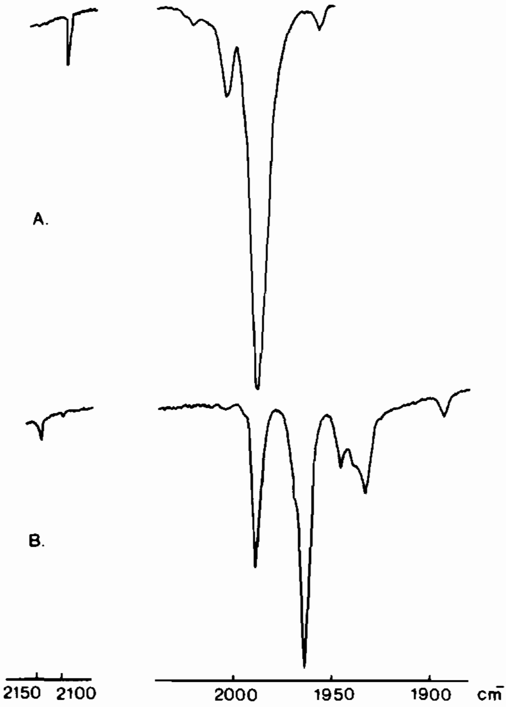

Figure 1. Infrared spectrum of $Cr(CO)_5PCl_3$ in an Ar matrix at 10 K. A. After deposition (S/M = 1/5200; pulse technique). B. After 960 nm photolysis with $\lambda = 313$ nm.

Irradiation of $Cr(CO)_5PCl_3$ in an argon matrix at 10 K with UV light (λ = 229, 254, 280, 313, 366 nm or an unfiltered Hg lamp) afforded two new IR bands in the CO stretching region. Comparing these results with those obtained by Turner *et al.* [9], the bands were assigned to the e and a_1 modes of the $Cr(CO)_5$ fragment. Besides $Cr(CO)_5$, free PCl_3 could be detected [10]. The reaction is reversed by subsequent irradiation with $\lambda = 436$ nm. After long periods of irradiation even $Cr(CO)_4$ and free CO proved to be present. Formation of $Cr(CO)_4PCl_3$ from $Cr(CO)_5PCl_3$, however, could never be observed. The same results have been found for $W(CO)_5PCl_3$ [10] and $W(CO)_5PF_3$ [11]. Photolysis of all these phosphorus complexes yielded $M(CO)_5$, independent of the wavelength.

Codeposition of analytically pure $Cr(CO)_5$pyrazine with argon always caused a very small, although detectable decomposition of $Cr(CO)_5$pyrazine into $Cr(CO)_6$ (Figure 2). Irradiation of $Cr(CO)_5$ pyrazine in the lowest ligand field transition resulted in the formation of $Cr(CO)_5$. The same formation was found by irradiating in the metal to pyrazine charge transfer transition at 463 nm.

Irradiation of $Cr(CO)_5$pyrazine with $\lambda = 229$ and 254 nm gave a four band pattern: 2037, 1923, 1912, 1885 cm^{-1}, as expected for the *cis* form of $Cr(CO)_4$ pyrazine together with the free CO modes (Figure 3).

Explanation of this difference in photochemical behaviour must take into account the relative energies

---

*To whom correspondence should be addressed.

TABLE. Infrared Frequencies (cm^{-1}) and UV–Visible Wavelengths (nm) of $Cr(CO)_5PCl_3$ and $Cr(CO)_5$pyrazine.

	A_1	B_1	A_1	E
$Cr(CO)_5PCl_3$ (Ar matrix, 10 K)	2093.6	2024.3	2005.9	1987.0
$Cr(CO)_5$pyrazine (Ar matrix, 10 K)	2074.0	1964.4	1934.8	1947.8
	$d \rightarrow \pi^*(CO)$	$d \rightarrow \pi^*(CO)$	$d \rightarrow \pi^*(L)$	$d \rightarrow d(S\text{–}S)$
$Cr(CO)_5PCl_3$ (n-heptane, RT)	227	287	252	362
$Cr(CO)_5$pyrazine (iso-octane, RT)	244	290	463	403

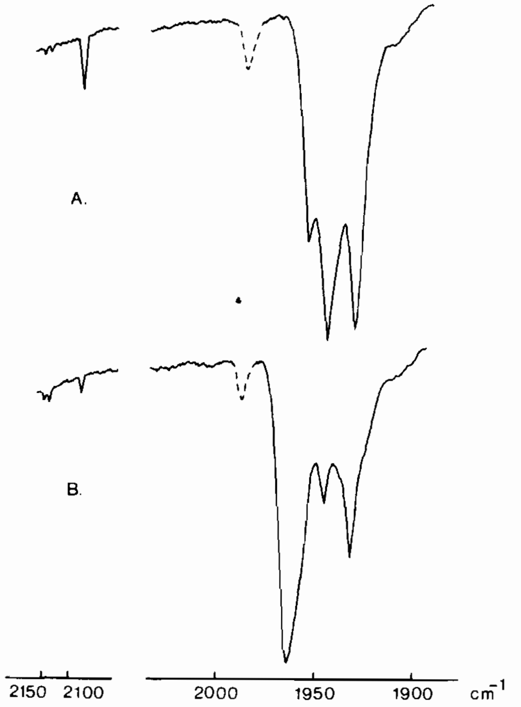

Figure 2. Infrared spectrum of $Cr(CO)_5$pyrazine in an Ar matrix at 10 K. A. After codeposition (--- = $Cr(CO)_6$). B. After 145 min photolysis with λ = 366 nm.

of the σ-antibonding d_{z^2} and $d_{x^2-y^2}$ orbitals [12, 13]. The d_{z^2} orbital in $M(CO)_5L$ molecules is always lower in energy than the $d_{x^2-y^2}$ orbital [14]. Short wavelength irradiation (λ = 229 and 254 nm) will result in the occupation of the $d_{x^2-y^2}$ orbital, causing loss of primarily CO and formation of *cis* $Cr(CO)_4$-pyrazine. Photolysis in lower excited states results in the population of the d_{z^2} orbital or in the population of the metal to pyrazine charge transfer state. Subsequently the formation of $Cr(CO)_5$ has been detected. At this stage of our study the conclusion drawn by Wrighton [4], that irradiation in metal to ligand L charge transfer transitions shows a significant smaller photochemical reactivity than irradiation in ligand field transitions cannot be subscribed.

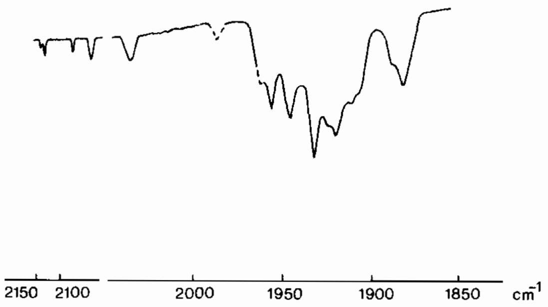

Figure 3. Infrared spectrum of $Cr(CO)_5$pyrazine in an Ar matrix at 10 K after 70 min photolysis with λ = 229 nm.

From UV–PES and UV spectra of $M(CO)_5PCl_3$ (M = Cr, W) it is deduced that the energy difference between the d_{z^2} and $d_{x^2-y^2}$ orbitals is smaller than in nitrogen donor complexes [10]. Because of this, occupation of the $d_{x^2-y^2}$ orbital can result in a fast nonradiative decay to the d_{z^2} orbital and loss of PCl_3 is observed. These results, however, can also be explained by assuming that not the $d_{x^2-y^2}$ orbital, but the measured metal to PCl_3 charge transfer state is occupied and that this state is the reactive state at short wavelength irradiation.

Acknowledgements

The authors express their thanks to Dr. D. J. Stufkens for helpful discussions. Drs H. Daamen is thanked for preparing the $Cr(CO)_5$pyrazine complex, H. Luyten and G. C. Schoemaker for their assistance.

References

1 M. Wrighton, G. S. Hammond and H. B. Gray, *Mol. Photochem.*, *5*, 179 (1973).

2 M. Wrighton, *Inorg. Chem.*, *13*, 905 (1974).

3 M. Wrighton, *Chem. Rev.*, *74*, 401 (1974).

4 M. Wrighton, H. B. Abrahamson and D. L. Morse, *J. Am. Chem. Soc.*, *98*, 4105 (1976).

5 M. Poliakoff, *Inorg. Chem.*, *15*, 2022 (1976).

6 M. Poliakoff, *Inorg. Chem.*, *15*, 2892 (1976).

7 J. D. Black and P. S. Braterman, *J. Organometal. Chem.*, *63*, C19 (1973).

8 A. J. Rest and J. R. Sodeau, *Chem. Comm.*, 696 (1975).

9 M. A. Graham, M. Poliakoff and J. J. Turner, *J. Chem. Soc. A*, 2939 (1971).

10 G. Boxhoorn and A. Oskam, *Inorg. Chim. Acta*, accepted for publication.

11 G. Boxhoorn and A. Oskam, unpublished results.

12 H. Daamen, G. Boxhoorn and A. Oskam, *Inorg. Chim. Acta*, *28*, 265 (1978).

13 H. Daamen and A. Oskam, *Inorg. Chim. Acta*, *26*, 81 (1978).

14 H. Daamen and A. Oskam, to be published.