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Photoreactions of $W(CO)_5$pyridine in an Ar Matrix at 10 K. Evidence for the Formation of C_s-$W(CO)_4$-pyridine after Short Wavelength Photolysis

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Photolysis of $W(CO)_5$pyridine in an Ar matrix at 12 K with 320 nm $< \lambda <$ 390 nm resulted in the rupture of the ligand, indicating that bulky ligands can be generated in matrices [1, 2]. The same was found for $W(CO)_5PCl_3$ [3], independent of the wavelenght of irradiation. Photolysis of $Cr(CO)_5L$ complexes (L = pyridine, pyrazine or NMe_3) however was shown to be dependent on the wavelength of irradiation and two complexes were observed for the first time in matrices [4, 5]:

$$Cr(CO)_5L \underset{\lambda\,=\,546\ \text{nm}}{\overset{\lambda\,\geqslant\,366\ \text{nm}}{\rightleftarrows}} Cr(CO)_5 + L$$

$$Cr(CO)_5L \underset{\lambda\,=\,546\ \text{nm}}{\overset{\lambda\,\leqslant\,313\ \text{nm}}{\rightleftarrows}} C_s\text{-}Cr(CO)_4L + CO$$

This photochemical behaviour was explained by a one electron d-orbital energy diagram. Long wavelength photolysis results in occupation of the d_{z^2} σ antibonding orbital and formation of $Cr(CO)_5$ and free ligand (L) is the result. Short wavelength photolysis results in occupation of the σ^* $d_{x^2-y^2}$ orbital and labilization along the x and y axis, yielding C_s-$Cr(CO)_4L$ and free CO. In contrast photolysis of $Cr(CO)_5PCl_3$ appeared to be wavelength independent. From the combination of UV–visible and PES data it was deduced that in the case of the PCl_3 complex, the energy difference between the $d_{x^2-y^2}$ and d_{z^2} orbitals is low. This small energy difference makes a fast non-radiative decay from the $d_{x^2-y^2}$ to the d_{z^2} orbital possible and only rupture of the ligand PCl_3 was found. From $W(CO)_5$pyridine, even irradiated between 320 and 390 nm, no traces of other photoproducts were detected. In this study we describe the short wavelength photolysis of $W(CO)_5$pyridine (λ = 229 and 254 nm) and we find evidence for the formation of C_s-$W(CO)_4$pyridine.

Short wavelength photolysis (λ = 229 and 254 nm) resulted in the formation of free CO and C_s-$W(CO)_4$-pyridine, deduced from the four new CO stretching bands at 2033.1, 1912.9, 1906.2 and 1879.6 cm^{-1} (3 A′ + A″) (see Fig. 1 and Table I).

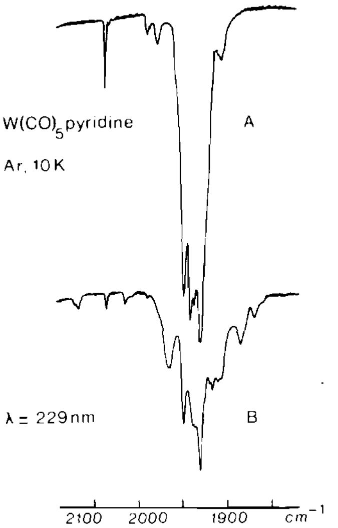

Fig. 1. Infrared spectrum of $W(CO)_5$pyridine in an Ar matrix at 10 K. A) After deposition. B) After 100 min photolysis with λ = 229 nm.

TABLE. Infrared Frequencies in cm^{-1}

Assignments	A_1	B_1	$E + A_1$	$E(^{13}CO)$
C_{4v}-$W(CO)_5$pyridine Ar matrix, 10 K	2076.8	1974.7	1947.2 1939.9 1933.9 1926.9	1902.6
Assignments	A_1	E	A_1	
C_{4v}-$W(CO)_5$, Ar matrix, 10 K	2097.3	1962.4	not observed	
Assignments	A′	A′	A′	A″
C_s-$W(CO)_4$pyridine Ar matrix, 10 K	2033.1	1912.9	1906.2	1879.6

These bands closely correspond to the bands measured for C_s-$Cr(CO)_4$pyridine: 2032.2, 1915.9, 1907.8 and 1881.5 cm^{-1} (split into 1884.6 and 1878.3 cm^{-1}). In contrast to the results with the $Cr(CO)_5$pyridine complex, almost the same quantum yield was found for the formation of $W(CO)_5$ (2097.3 and 1962.8 cm^{-1}) after short wavelength photolysis.

The third band (A_1) of $W(CO)_5$ at about 1931 cm^{-1} was obscured by parent bands. Solution photochemistry has already shown that the quantum yield for loss of CO occurred with a very low efficiency, even after irradiation at $\lambda = 254$ nm [6]:

$$W(CO)_5\text{pyridine} \xrightarrow{\phi_L} W(CO)_5 + \text{pyridine}$$

$$W(CO)_5\text{pyridine} \xrightarrow{\phi_{CO}} W(CO)_4\text{pyridine} + CO$$

$\phi_L = 0.63$ at $\lambda = 436$ nm and 0.34 at $\lambda = 254$ nm.

$\phi_{CO} = 0.002$ at $\lambda = 436$ nm and 0.04 at $\lambda = 254$ nm in iso-octane–pent-1-ene (2:1 v/v).

The high quantum yield of $W(CO)_5$ formation can be explained by increased non-radiative decay from the $d_{x^2-y^2}$ to the excited d_{z^2} orbital in going from $Cr(CO)_5$pyridine to $W(CO)_5$pyridine. The result is an increased loss of the ligand pyridine. This increased non-radiative decay may be caused by the increased spin–orbit coupling for the $W(CO)_5$pyridine complex. The same was found for the photolysis in Xe matrices; externally enhanced spin–orbit coupling resulted in low quantum yields and fast non-radiative decays [5, 7]. This is illustrated by the phosphorescence lifetime (τ_p) for C_6H_6 in matrices at 10 K. This lifetime is very much shorter for Xe, than for Ar (0.02 *versus* 14.4 sec) and fluorescence is entirely quenched in Xe, whereas the fluorescence in Ar can be measured (46 msec) [7]. It should also be noticed that in the series $M(CO)_5$pyridine (M = Cr, Mo, W) the Mo and W complexes show luminescence after irradiation into the ≃400 nm bands (d–d transition), whereas the Cr complex does not luminesce [8].

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References

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

2 T. M. McHugh, A. J. Rest and J. R. Sodeau, *J. Chem. Soc. Dalton*, 184 (1979).

3 G. Boxhoorn and A. Oskam, *Inorg. Chim. Acta, 29*, 243 (1978).

4 G. Boxhoorn, D. J. Stufkens and A. Oskam, *Inorg. Chim. Acta, 33*, 215 (1979).

5 G. Boxhoorn, D. J. Stufkens and A. Oskam, to be published.

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

7 E. P. Gibson, R. Narayanaswamy, A. J. Rest and K. Salisbury, in preparation and unpublished results.

8 T. M. McHugh, R. Narayanaswamy, A. J. Rest and K. Salisbury, *Chem. Comm.*, 208 (1979).