Kinetics and Mechanism of a Photogenerated $W(CO)_5L$ Intermediate, where L = 2-Pyridinal-imine Ligand

LISA CHAN and ALISTAIR J. LEES*

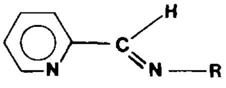
Department of Chemistry, State University of New York at Binghamton, Binghamton, N.Y. 13901, U.S.A.

Received August 16, 1985

Although ligand photosubstitution processes of metal carbonyl complexes have been extensively studied [1] relatively little is known about the reactivity of their intermediates in solution [2]. Direct spectral evidence for these intermediates has rarely been reported. Most studies have been concerned with $M(CO)_5$ (M = Cr, Mo, W) intermediates formed following light irradiation of the parent hexacarbonyls [3]. The $M(CO)_5$ intermediate has been shown to be an extremely reactive species in solution coordinating with even weak donors at rates approaching the diffusion limit [4]. In the presence of an excess concentration of diimine ligand photolysis leads to production of $M(CO)_4$(diimine) (see eqn. (1)) [5]. Presumably this reaction proceeds via a monodentate intermediate.

$$M(CO)_6 \xrightarrow[\text{diimine}]{h\nu} M(CO)_4(\text{diimine}) + 2CO \qquad (1)$$

This paper reports electronic absorption spectral evidence for a monodentate intermediate formed following photolysis of $W(CO)_6$ with 2-pyridinal-imine (py–R–im) ligands. Details of the kinetic and mechanistic behavior of the subsequent chelation reaction of $W(CO)_5$(py–R–im) are presented.



R = Ph, t-Bu

py-R-im

Experimental

The 2-pyridinal-imine ligands were prepared essentially as previously described by the 1:1 condensation of 2-pyridinecarboxaldehyde and primary amine [6]. Tetracarbonyl complexes were synthesized and isolated according to procedures previously reported [7].

In a typical experiment 5×10^{-4} M $W(CO)_6$ and 10^{-2} M diimine in deoxygenated benzene was irradiated for 5 s with a 200 W Hg lamp. Approximately 1×10^{-4} M $W(CO)_6$ is photodissociated during this photolysis; this value was estimated from the known quantum efficiency of $W(CO)_6$ [8] and a determination of the incident light intensity using Ferrioxalate actinometry [9]. This value was confirmed at the end of the kinetic experiment from the amount of $W(CO)_4L$ product formed. Electronic absorption data were obtained on a spectrophotometer which incorporates a microprocessor-controlled diode-array detector; the shortest acquisition time interval possible on this apparatus is 1 s. The initial spectrum was recorded within 2 s after excitation and subsequent spectra were recorded at suitable time intervals thereafter. Benzene used in the kinetic procedures was obtained as spectroscopic grade and further purified by absorptive filtration through Woelm basic alumina of activity grade 1. Nitrogen used for purging was ensured to be dry and deoxygenated using a method described previously [10].

Results and Discussion

Figure 1 illustrates the sequence of UV–Vis spectra recorded at 298 K following 5 s irradiation of 5×10^{-4} M $W(CO)_6$ in benzene containing 10^{-2} M 2-pyridinal-phenylimine (py–Ph–im). Following an immediate absorbance increase at ~400 nm, the reaction proceeds to form $W(CO)_4$(py–Ph–im) product as evidenced by the growth of its characteristically intense metal to ligand charge-transfer (MLCT) absorption centered at 574 nm. This reaction appears to proceed cleanly maintaining a sharp isosbestic point at 482 nm. Similar spectral results were obtained for the corresponding reaction involving L = 2-pyridinal-t-butylimine (py–t-Bu–im) with the MLCT absorption of product at 534 nm and an isosbestic point at 430 nm. The $M(CO)_4L$ complexes were isolated (see Experimental) and their UV–Vis spectra were coincident with the final absorption obtained in the kinetic experiment. The following eqns. (2)–(3), are consistent with the experimental observations.

$$W(CO)_6 \xrightarrow[\text{(py–R–im)}]{h\nu} W(CO)_5(\text{py–R–im}) + CO \qquad (2)$$

$$W(CO)_5(\text{py–R–im}) \xrightarrow{\Delta} W(CO)_4(\text{py–R–im}) + CO \qquad (3)$$

Figure 2 shows the difference UV–Vis spectrum obtained by subtracting the absorption data of the unphotolyzed solution containing $W(CO)_6$ and Py–Ph–im from the spectrum recorded immediately

---

*Author to whom correspondence should be addressed.

0020-1693/86/$3.50

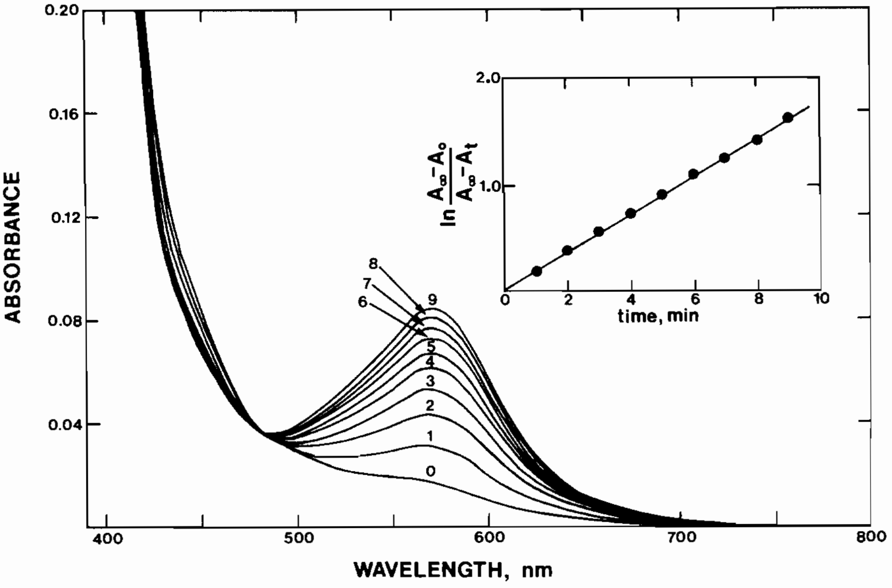


Fig. 1. Spectral sequence recorded following 5 s photolysis of 5 $\times 10^{-4}$ M $W(CO)_6$ and 10^{-2} M 2-pyridinal-phenylimine in benzene at 298 K. Curve 0: initial spectrum recorded within 2 s after excitation. Curves 1–9: subsequent spectra at 1 min time intervals. Inset illustrates time dependent behavior of absorption at 574 nm.

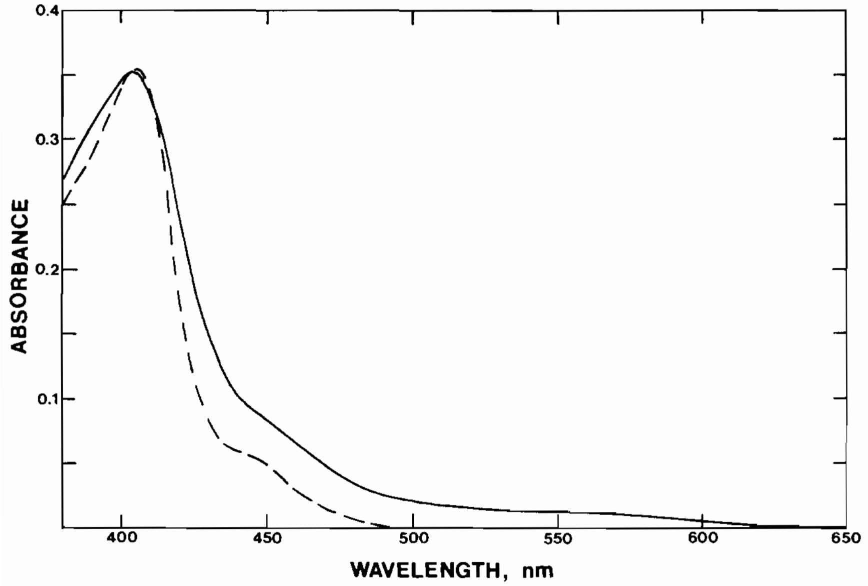


Fig. 2. Difference absorption spectrum (——) obtained by subtracting spectral data of unphotolysed solution from curve 1 of Fig. 1. For comparison the spectral features of $W(CO)_5$(piperidine) are included (– – –); absorption is scaled arbitrarily to make maxima equal.

following excitation. These spectral features, representing the initially photoproduced intermediate, are attributed to $W(CO)_5$(py–Ph–im), where the normally bidentate ligand is coordinated in a monodentate manner. Further evidence for the monodentate character of this intermediate is obtained from a comparison with $W(CO)_5$(piperidine). Hence, the absorption features of $W(CO)_5$(py–Ph–im) in benzene at 404 nm and 450 nm (sh) are assigned to $^1A \rightarrow {}^1E$ and $^1A \rightarrow {}^3E$ ligand-field transitions, respectively [11]. The weak absorption centered at 574 nm is due to a small amount of $W(CO)_4$(py–Ph–im) formed during the irradiation and before the first reading. Similar $^1A \rightarrow {}^1E$ and $^1A \rightarrow {}^3E$ features

TABLE I. Temperature Depencence of Rate Constants and Calculated Activation Energy Parameters for the Reaction of $W(CO)_5$-L to form $W(CO)_4L$ and CO

Py–Ca–R Ligand	Temperature (K)	k_{obs} (s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol)
R = Ph	283	1.08×10^{-3}	45.6(±8.0)	–140.2(±16.0)
	288	1.67×10^{-3}		
	293	1.97×10^{-3}		
	298	2.97×10^{-3}		
	303	4.37×10^{-3}		
R = t-Bu	293	1.50×10^{-3}	82.0(±6.0)	–56.9(±12.0)
	303	5.30×10^{-5}		
	313	1.28×10^{-4}		
	323	4.04×10^{-4}		

were observed at 390 nm and 438 nm (sh) in the difference spectrum representing $W(CO)_5$(py–t-Bu–im).

Reaction rates have been measured for the chelation of these $W(CO)_5$(py–R–im) species. For each spectral sequence the rate was determined by monitoring the growth of the long wavelength MLCT absorption of $W(CO)_4$(py–R–im). The growth from A_0 to A_∞ is exponential and a plot of $\ln[(A_\infty - A_0)/(A_\infty - A_t)]$ *vs.* time is linear, yielding slope = k_{obs}. Here A_0 is defined as the initial absorbance, A_t is the absorbance at varying time, and A_∞ is the final absorbance reached; all absorbance values being recorded at fixed wavelength in the MLCT region. A representative plot is included in Fig. 1. Table I summarizes the first-order rate data obtained for eqn. (3). It is apparent that the reaction rate is highly dependent on the nature of ligand substituent. Furthermore, these rates of ring closure are substantially greater than those previously observed for thermal substitution of either CO or L in $M(CO)_5L$ complexes [12]. Several $M(CO)_5$(L–L) complexes (L–L = a bidentate P or As donor ligand) are known to undergo a relatively slow chelation process [13]. For instance, when M = W and L = $Ph_2PCH_2CH_2PPh_2$, $k_{obs} = 4.47 \times 10^{-6}$ s^{-1} at 123 °C and activation parameters have been reported as $\Delta H^{\neq}$ = 155 kJ mol^{-1} and $\Delta S^{\neq}$ = 40 J K^{-1} mol^{-1}. It has been concluded that these complexes undergo ring closure via a largely dissociative mechanism [13]. The rate data obtained in this study imply that a substantial contribution to the CO extrusion reaction is made by the associating ligand when it is already coordinated in a monodentate fashion. Apparently the bulky tertiary butyl groups effectively reduce the associative component of reaction. Calculated activation energy parameters (see Table I) further substantiate these conclusions. Activation enthalpy values are considerably lower than reported for release of CO from $W(CO)_6$ (167 kJ mol^{-1}) [14] or the above $W(CO)_5$(L–L) complexes [13]. Moreover, the negative entropy values are consistent with a degree of associative character in the reaction transition state; this is particularly so when L = py–Ph–im. The large ligand substituent dependence on reaction rate is under further investigation.

Acknowledgements

We thank the donors of the Petroleum Research Fund administered by the American Chemical Society, for support of this research and Prof. D. J. Stufkens for advice on the ligand synthesis.

References

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

2 D. J. Darensbourg, *Adv. Organomet. Chem., 21,* 113 (1982); J. A. S. Howell and P. M. Burkinshaw, *Chem. Rev., 83,* 557 (1983).

3 I. W. Stolz, G. R. Dobson and R. K. Sheline, *J. Am. Chem. Soc., 84,* 3589 (1962); I. W. Stolz, G. R. Dobson and R. K. Sheline, *J. Am. Chem. Soc., 85,* 1013 (1963); M. A. Graham, M. Poliakoff and J. J. Turner, *J. Chem. Soc. A,* 2939 (1971); R. N. Perutz and J. J. Turner, *J. Am. Chem. Soc., 97,* 4791 (1975); D. R. Tyler and D. P. Petrylak, *J. Organomet. Chem., 212,* 389 (1981).

4 A. J. Lees and A. W. Adamson, *Inorg. Chem., 20,* 4381 (1981); J. M. Kelly, C. Long and R. Bonneau, *J. Phys. Chem., 87,* 3344 (1983); S. P. Church, F.-W. Grevels, H. Hermann and K. Schaffner, *Inorg. Chem., 23,* 3830 (1984).

5 W. Strohmeier, *Angew. Chem., 76,* 873 (1964).

6 G. Bahr and H. Thamlitz, *Z. Anorg. Allg. Chem., 282,* 3 (1955).

7 H. Bock and H. tom Dieck, *Angew. Chem., 78,* 549 (1966); H. Bock and H. tom Dieck, *Chem. Ber., 100,* 228 (1967); H. Brunner and W. A. Herrmann, *Chem. Ber., 105,* 770 (1972); D. M. Manuta and A. J. Lees, *Inorg. Chem., 22,* 3825 (1983).

8 W. Strohmeier and D. von Hobe, *Chem. Ber., 94,* 761 (1961).

9 C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A, 235,* 518 (1956).

10 M. J. Schadt, N. J. Gresalfi and A. J. Lees, *Inorg. Chem., 24,* 2942 (1985).

11 M. S. Wrighton, H. B. Abrahamson and D. L. Morse, *J. Am. Chem. Soc., 98,* 4015 (1976).

12 D. J. Darensbourg and T. L. Brown, *Inorg. Chem., 7,* 1679 (1968); C. M. Ingemanson and R. J. Angelici, *Inorg. Chem., 7,* 2646 (1968); W. D. Covey and T. L. Brown, *Inorg. Chem., 12,* 2820 (1973).

13 J. A. Connor, J. P. Day, E. M. Jones and G. K. McEwen, *J. Chem. Soc., Dalton Trans.,* 347 (1973); J. A. Connor and G. A. Hudson, *J. Organomet. Chem., 73,* 351 (1974); J. A. Connor and P. I. Riley, *J. Organomet. Chem., 94,* 55 (1975).

14 J. R. Graham and R. J. Angelici, *Inorg. Chem., 6,* 2082 (1967).