Pulsed Laser Flash Photolysis with IR Diode Laser Detection: the Reaction of Photogenerated *trans*-[(n-C$_7$H$_{16}$)(P(OPr^i)$_3$)W(CO)$_4$] with Piperidine*

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Abstract

Pulsed laser flash photolysis with IR detection apparatus in which the analyzing source is an IR diode laser has been used to study ligand-exchange reactions of metal carbonyl transients in solution. The apparatus is described and the advantages of the IR diode laser analyzing source over the 'globar' and line-tuneable CO laser sources previously employed in such studies are discussed. It has been employed to monitor the thermal reaction with pip of *trans*-[(n-C$_7$H$_{16}$)(L)W(CO)$_4$], (L = tri(isopropyl) phosphite) produced via pulsed laser flash photolysis of *cis*-(pip)(L)W(CO)$_4$ in n-heptane. This reaction obeys a mixed order rate law interpreted in terms of bimolecular 'trapping' of the photogenerated intermediate with pip to afford *trans*-(pip)(L)W(CO)$_4$ and a competing unimolecular pathway tentatively ascribed to slow isomerization of *trans*-[(L)W(CO)$_4$] to its *cis* analogue. This isomer then is rapidly trapped by pip to afford the *cis*-(pip)(L)W(CO)$_4$ photolysis precursor.

Since its development by Norrish and Porter [1], the flash photolysis technique has been employed to probe the nature of many reactive chemical species in solution. Because of the sensitivity and response times of UV and visible detectors, most applications of flash photolysis have employed UV or visible analysing beams. However, in large molecules, the relatively featureless UV–Vis spectra provide little information with regard to the identities and structures of the photogenerated species [2]. Recently, however, flash photolysis with infrared detection in solution (FP/IR) has been employed to provide such information for metal carbonyls and derivatives by probing the intense carbonyl stretching chromophores [3]. These studies have employed either CO laser analysing beams [4], or conventional 'globar' IR

sources [5]. The former provides an intense IR beam, but over only a limited frequency range (2010–1750 cm^{-1}). Moreover, the CO laser is 'line-tuneable' with resolution of *ca.* 8 cm^{-1} because the vibrational–rotational spacings in CO are *ca.* 4 cm^{-1}. Taking data for both CO and ^{13}CO gas fills, resolution of 4 cm^{-1} can be obtained. The globar source, while providing a continuum in the infrared, affords an IR beam of low power which results in a poor signal-to-noise ratio even at relatively low resolution. On the other hand, tuneable IR diode laser sources would appear to offer the potential for significantly greater power coupled with high resolution over the entire IR spectral range [6]. As a preliminary test of the efficacy of employing IR diode laser detection in an FP/IR system, the reaction of the well-characterized *trans*-[(n-C$_7$H$_{16}$)(P(OPr^i)$_3$)W(CO)$_4$] [7] (**1-I$_1'$**) with piperidine, which takes place by the reaction scheme given in Fig. 1, has been investigated[†]. The frequency of the most intense carbonyl stretching absorption in **1-I$_1'$**, of E_u symmetry presuming D_{4h} local symmetry for the four carbonyls, was monitored at 1907 cm^{-1}. This species was one of those generated upon flash photolysis of *cis*-(pip)(P(OPr^i)$_3$)W(CO)$_4$ (**1-R**) in n-heptane.

Figure 2 presents block diagrams for the equipment employed. In Fig. 2a, the IR probe beam leaves the diode laser spectrometer (Laser Analytics Model LS-3), passes through an iris (I$_1$) and the 1 mm NaCl sample cell (S), is reflected from a pair of mirrors (MP) and is returned through a second iris (I$_2$) to the monochromator (MC) of the LS-3 spectrometer. Upon leaving the monochromator, the beam passes through a short focal length BaF$_2$ lens (L$_1$) which focusses the probe beam through a ZnSe filter (F$_1$) onto the InSb detector (D; 0.1 microsecond time

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[†]The corresponding *cis*-isomer, (**1-I$_1$**), is also produced upon photolysis. The second-order rate constant for its combination with pip was found to be $> 7.4 \times 10^7$ M^{-1} s^{-1} by monitoring the decay of a carbonyl stretching band attributable to it (ref. 7) at 1916 cm^{-1}; this rate was too fast to measure accurately with the equipment employed here (*vide infra*).
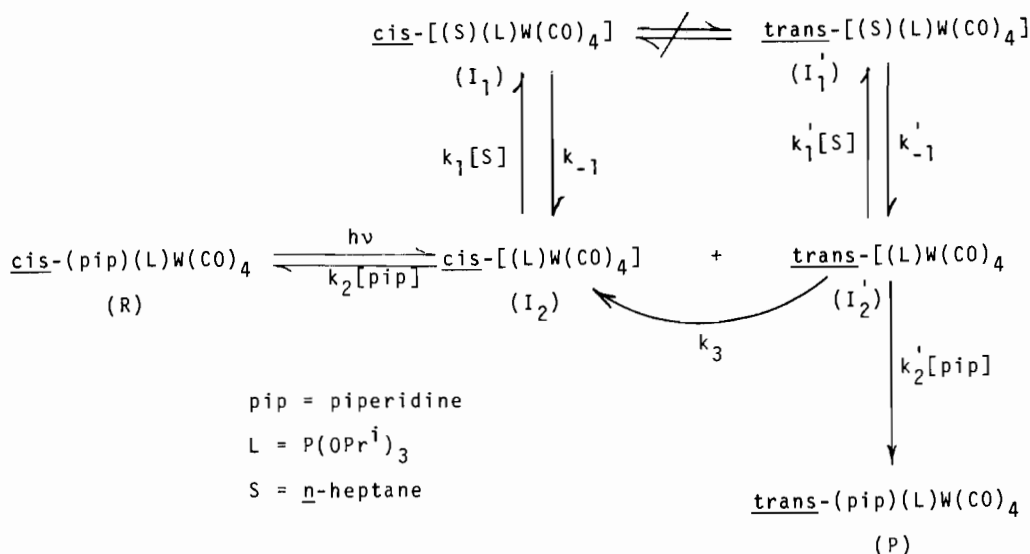
Fig. 1. Reaction scheme for flash photolysis of cis-(pip)(P(OPr^i)$_3$)W(CO)$_4$ with pip (piperidine) in n-heptane.
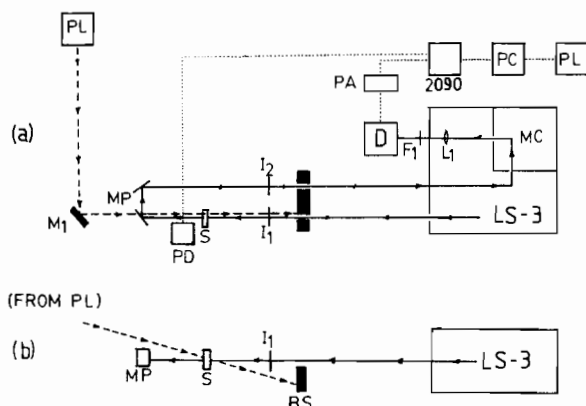

Fig. 2. Schematics for pulsed laser flash photolysis with IR diode laser detection instrumentation.

constant; Barnes Engineering Co.). The detector preamplifier, (PA; Perry 730HF) was connected to a Nicolet 2090 digital oscilloscope via a 50 ohm termination. The detector/preamplifier time constant is *ca.* 0.5 microseconds. The digital oscilloscope was interfaced to an IBM PC microcomputer and a Hewlett-Packard 7470A plotter (PL). A photodiode (PD) responding to scattered light from the photolysis flash triggered the detection system.

The photolysis source (PL) was either a Nd:YAG laser (Molectron MY-34) operating at 355 nm (*ca.* 100 mJ/pulse, 15–20 ns FWHI) or an excimer laser (Lambda Physik 150 EST) operating at 308 nm (*ca.* 125 mJ/pulse, 15–30 ns FWHI). The photolysis beam was directed by a mirror (M$_1$) through the sample cell and into a beamstop (BS). The diameter of the probe beam was less than that of the photolysis beam and it was essential that the photolysis pulse have uniform density in the region intersected by the IR probe.

Figure 3 illustrates a typical 'single shot' plot of absorbance *versus* time for the disappearance of 1−R in its reaction with pip at ambient temperature monitoring 1907 cm^{-1}. 1-I$_1'$ has been identified unequivocally as the species absorbing at 1907 cm^{-1} through FP/IR studies (CO laser analysing beam) of 1-R in n-heptane [7]. The initial oscillation is attributable to detection of the scattered laser flash. It can be seen that a signal-to-noise ratio of about 10 is achieved. Computer-averaging of four or more 'shots' for data at four different concentrations of pip over the concentration range 0–25 mM afforded the plot of the pseudo first-order rate constants, k_{obs} *versus* [pip], shown in Fig. 4. The data afford the rate constants, k_{app} (from the intercept) of 2.70×10^4 s^{-1} and k'_{app} (from the slope) of 3.63×10^6 M^{-1} s^{-1}; the correlation coefficient is 0.998.

The intercept is likely attributable to isomerization of 1-I$_2'$ to its *cis* analogue, (1-I$_2$), governed by k_3, Fig. 1, followed by rapid reaction of 1-I$_2$ with pip to afford 1-R. An increase in absorbance at 1889 cm^{-1}, barely above background noise, which could be attributable to the formation of 1-R [7] from 1-I$_2'$ is noted, although unimolecular decomposition of I-I$_2'$ cannot be ruled out*.

The rate constant, k'_{app}, obtained from the slope, is $k_{-1}k_2'/k_1'$[n-heptane], as derived from eqn. (1) through the assumption that k_1'[n-heptane] $\gg$ k_2'[pip], reasonable in that it is to be expected that $k_1' \approx k_2'$ (*vide infra*). The reaction product is *trans*-(pip)(P(OPr^i)$_3$)W(CO)$_4$ (1-P) which must undergo subsequent reaction or isomerization, since no *trans*-

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*Evidence has been presented for related species [14] which suggests such decomposition to be possible even in the presence of 'trapping agents' such as CO.
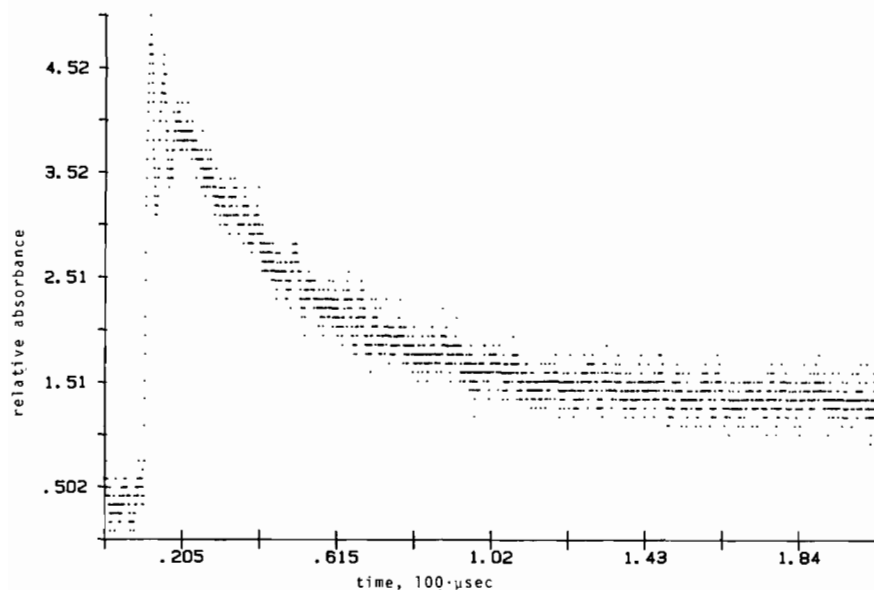
Fig. 3. Plot of absorbance *vs.* time (1907 cm^{-1}) after flash photolysis of *cis*-(pip)(P(OPr^i)$_3$)W(CO)$_4$ with pip (piperidine) in n-heptane at ambient temperature.
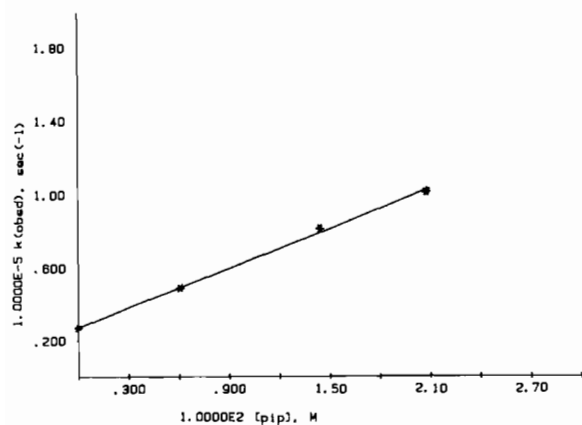

Fig. 4. Plot of k_{obs} *vs.* [pip] for reaction of the photogenerated *trans*-[(P(OPr^i)$_3$)W(CO)$_4$] intermediate with piperidine in n-heptane at ambient temperature.

(amine)(L)W(CO)$_4$ complex has ever been isolated [8]. The rate constant observed is very reasonable when compared to that for the reaction of 1-I$_1'$ with CO, 1.8 × 10^6 M^{-1} s^{-1} [7]. Recent flash photolysis studies of *cis*-[(CB)(P(OPr^i)$_3$)W(CO)$_4$] (1-I$_1$) in cyclohexane/CB/pip solutions (CB = chlorobenzene) have demonstrated that the CB 'solvent' is displaced by pip from 1-I$_1$ via a mechanism which involves initial CB dissociation [9]. Thus the species which reacts with pip is the 'naked' five-coordinate intermediate, *trans*-[(P(OPr^i)$_3$)W(CO)$_4$], (1-I$_2'$). Based on studies of related intermediates such as [Cr(CO)$_5$] in both the gas phase and in solution [10], species such as 1-I$_2'$ are expected to be very reactive, and, consequently, to possess little discriminating ability among incoming nucleophiles. This has been demonstrated to be the case for 1-I$_2$ in its reactions with pip and a variety of phosphines and phosphites; the observed reaction rates in these systems vary by less than three-fold [9].

While the overall performance of the equipment is thus far satisfactory, there exist areas in which significant improvement could be made, particularly in sample cell design, analysing beam optics and the determination of absolute transmittance values. The results indicate that flash photolysis with IR diode laser detection has the potential to develop into a means of obtaining IR spectra of acceptable signal-to-noise ratios and resolution* not only of photogenerated transients containing the terminal carbonyl chromophore, but also containing transients containing other intense chromophores of interest to inorganic chemists within the frequency range of 350–3500 cm^{-1}, such as the Si–H [11], C=O [12] and cyanide [13] stretching modes.

Acknowledgements

*See 'Note Added in Proof', p. 94.

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Note Added in Proof

Since this paper was submitted, two other reports of FP/IR equipment utilizing IR diode laser analyzing beams monitoring $\nu(Co)$ (in systems of biological significance) have appeared in the literature: (a) A. Ansari, J. Berendzen, D. Braunstein, B. R. Cowen, H. Frauenfelder, M. K. Hong, I. E. T. Iben, J. B. Johnson, P. Ormos, T. B. Sauke, R. Scholl, A. Schutte, P. J. Steinbach, J. Vittitow and R. D. Young, *Biophys. Chem.*, *26*, 337 (1987); (b) J. N. Moore, P. A. Hansen and R. M. Hochstrasser, *Chem. Phys. Lett.*, *138*, 110 (1987).