Dynamics of Intermediates in the α- and β-Elimination Processes in $CpW(CO)_2Me$ and $CpW(CO)_2Et$

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Abstract: Picosecond flash photolysis of $CpW(CO)_3R$ (R = Me, Et) in cyclohexane solution shows that the unsaturated CO loss products $CpW(CO)_2R$ are formed within 25 ps after photolysis. In microsecond flash photolysis studies when R = Et, the intramolecular hydrogen bound intermediate formed by coordination of the ethyl group β-hydrogen to the metal is formed with a rate constant $k_1 = 1.5 \pm 0.8 \times 10^5\ s^{-1}$ ($\Delta G_1 = 10.8 \pm 0.4$ kcal/mol assuming a preexponential factor of $10^{13}\ s^{-1}$). Subsequent β-elimination is observed and an upper bound of 12.3 ± 0.4 kcal/mol can be placed on the activation energy for this process. When $CpW(CO)_3Me$ is photolyzed in cyclohexane with 0.02–1.0 M THF the initially formed $CpW(CO)_2Me$ is coordinated by THF followed by the formation of a new intermediate. The degree to which this reaction occurs is inversely dependent on [THF] while the rate of the reaction is independent of [THF]. A mechanism is proposed that explains these observations and suggests that the new product arises from α-elimination.

A prerequisite to the decomposition of organometallic alkyl complexes is considered to be the opening of a vacant coordination site on the metal by dissociation of a ligand such as CO.[1] Such ligand loss can be achieved either thermally or photochemically.[2] Laser flash spectroscopic techniques are particularly well suited for the generation of the initial unsaturated intermediates and real time observation of the steps subsequent to ligand dissociation. A recent study by Kazlauskas and Wrighton has examined the photolysis of $CpM(CO)_3R$ (M = Mo, W; R = Me, Et) in low-temperature matrices and reported on the visible absorption spectra of the thus formed intermediates.[3a] A study by Tyler has demonstrated by isolation of the substitution products $CpW(CO)_2(L)Me$ that loss of CO from $CpW(CO)_3Me$ occurs as the primary photoprocess in room temperature solution.[3b] Rest and Hooker have reported that the photolysis of $CpW(CO)_3Me$ in PVC film at 12 K does not induce homolytic cleavage of the W–Me bond.[3c] In this paper, we report our results of the picosecond and nanosecond dynamics of several transients formed upon room temperature photolysis of $CpW(CO)_3R$ (R = Me, Et) in cyclohexane solution.

Experimental Section

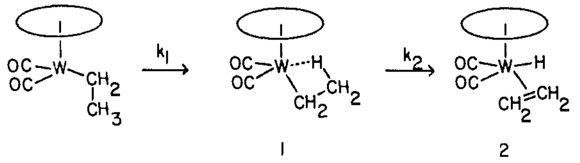
The picosecond absorption spectrometer has been described previously.[4] Nanosecond flash photolysis was achieved with the 308-nm line of a XeCl eximer laser (Lambda Physik EMG 101, 5 ns pulse duration, 1 mJ/pulse). A xenon flash lamp (EG+G FY-711) was used for interrogation. The detector consisted of a spectrograph (PAR 1225) interfaced to a gated OMA vidicon system (PAR 1215, 1216, 1211, 1254). Wavelengths between 400 and 620 nm were detectable. Time delays of 50 ns to several milliseconds between photolysis and detection were controlled by a Hewlett-Packard 214A pulse generator which was driven at 2 Hz by an HP 8013B pulse generator.

$CpW(CO)_3Me$ and $CpW(CO)_3Et$ were prepared by literature methods.[5] Solvents (THF, cyclohexane) were spectrophotometric grade and were used without purification.

The solutions of the appropriate tungsten complex (10^{-4} M) used for photolysis were flowed through a quartz cuvette at 2–3 mL/min. A typical experiment yielding data at five different time delays after photolysis would consume 100–200 mL of solution which was then discarded. Identical results were obtained whether the photolyses were run with solutions purged with argon or under aerobic conditions.

All spectra are reported as the difference in the absorbance of the sample before photolysis from that after photolysis. Thus, a positive absorbance implies increased absorbance upon photolysis.

Scheme I



Results

When cyclohexane solutions of either $CpW(CO)_3Me$ or $CpW(CO)_3Et$ are irradiated with a 25-ps pulse of 355-nm light from a mode-locked Nd-YAG laser a broad spectral feature is observed between 430 and 630 nm[6] (Figure 1) which appears similar for both complexes. These absorbances are formed within the duration of the laser pulse and exhibit no dynamics up to 125 ns after the laser flash. Kazlauskas and Wrighton have reported the initial photoproducts to have broad absorbances throughout the visible with an apparent absorption maximum near 600 nm in hydrocarbon glass at 77 K and have assigned these to the unsaturated $CpW(CO)_2R$ complexes.[3a] Therefore, we assign the intermediates we initially observe to be the CO loss products $CpW(CO)_2Me$ and $CpW(CO)_2Et$.

Although the initial photochemistry proceeds by the same process for both complexes, i.e., CO dissociation, subsequent chemistry observed on the nanosecond to microsecond time scales is quite different. When a cyclohexane solution of $CpW(CO)_3Et$ is photolyzed with a 5-ns pulse of 308-nm light in our nanosecond spectrometer a broad absorbance is observed in the region 400–620 nm 100 ns after the laser flash (Figure 2). This absorbance has the same general appearance as the transient observed in the picosecond experiment and so is assigned to be $CpW(CO)_2Et$.

The initial spectrum undergoes a rapid decay in the region near 565 nm. At 420 nm an initially rapid then slower decay occurs (Figure 2). Both decays exhibit no further change 500 μs after the laser pulse. The appearance of an absorption maximum near 400 nm is consistent with the decay of $CpW(CO)_2Et$ to the self-solvated structure **1** which has been identified to have λ_{max} at 405 nm.[3a] The second, slower decay is most likely the β-elimination step of **1** going to the *cis*-olefin hydride **2** (Scheme I).[7] The rate constants for the two processes are $k_1 = 1.5 \pm 0.8 \times 10^5\ s^{-1}$ and $k_2 = 1.1 \pm 0.6 \times 10^4\ s^{-1}$ corresponding to $\Delta G_1 = 10.8 \pm 0.4$ kcal/mol and $\Delta G_2 = 12.3 \pm 0.4$ kcal/mol when a preexponential factor of $10^{13}\ s^{-1}$ is assumed for a unimolecular process.[8] These barriers are somewhat larger than the "<10

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[2] Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.

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[4] Peters, K. S.; Freilich, S. C.; Schaeffer, C. G. *J. Am. Chem. Soc.* **1980**, *102*, 5701–5702.

[5] Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104–124.

[6] The limits of observable wavelengths for the picosecond and nanosecond spectrometers are 430–630 and 400–620 nm, respectively.

[7] Throughout this paper

$\equiv \eta^5$-C_5H_5

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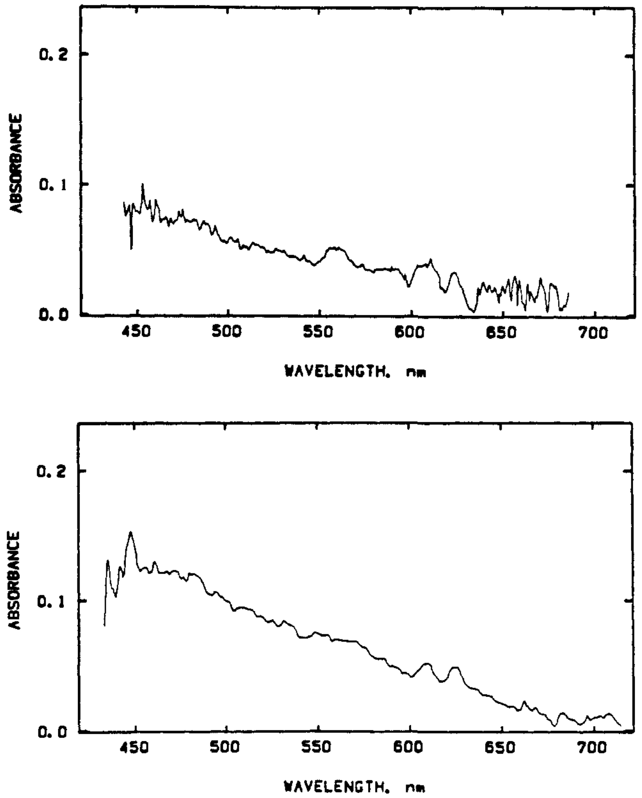


Figure 1. Difference absorption spectra recorded 25 ps after photolysis by 355-nm light of cyclohexane solutions of (a) $CpW(CO)_3Et$ and (b) $CpW(CO)_3Me$.

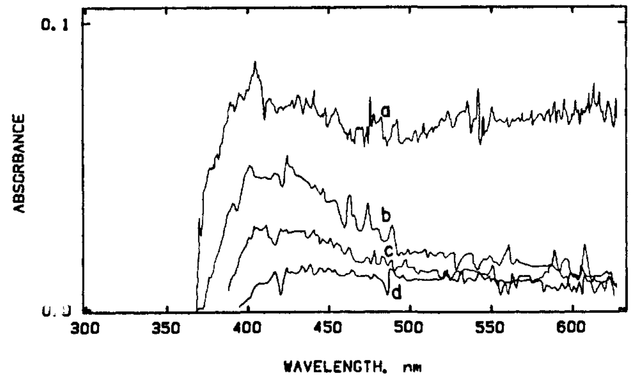


Figure 2. Difference absorption spectra recorded for the photolysis of a cyclohexane solution of $CpW(CO)_3Et$ at 308 nm. Spectra recorded (a) 100 ns, (b) 10 μs, (c) 100 μs, and (d) 500 μs after photolysis.

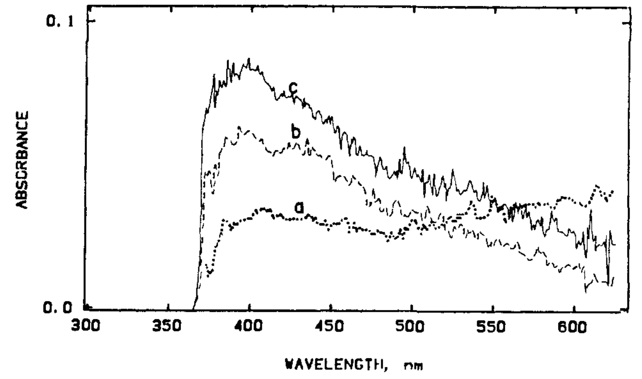


Figure 3. Difference absorption spectra recorded (a) 100 ns, (b) 10 μs, and (c) 100 μs after photolysis of a cyclohexane solution of $CpW(CO)_3Me$ with 308-nm light.

kcal/mol" estimated by Kazlauskas and Wrighton but are close enough within experimental error to be consistent with their model.

Table I

[THF], mol/L	$k_{obsd} \times 10^{-3}$,[a] s^{-1}	A_f/A_i[b]
0.00	72	
0.02	7.2	1.47
0.04	8.0	0.97
0.20	6.1	0.65
1.0	c	0.66

[a] ±50%. [b] (Final absorbance)/(absorbance at 100 ns) at 408 nm. [c] The rate is unmeasureable at this concentration due to the small change in absorbance.

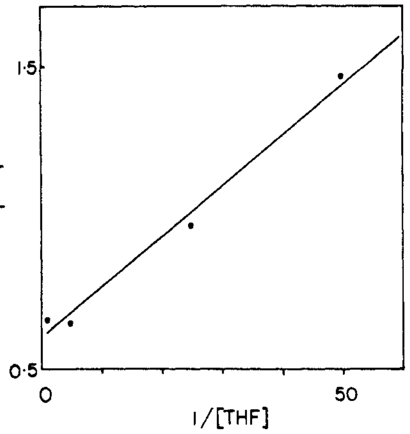
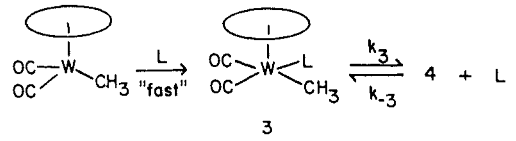


Figure 4. plot of the final absorbance normalized to the initial absorbance at 408 nm vs. 1/[THF]. Data are given in Table I.

Scheme II



When a cyclohexane solution of $CpW(CO)_3Me$ is photolyzed at 308 nm in the nanosecond spectrometer a broad absorption in the 400–620-nm region is again observed (Figure 3) and assigned to the unsaturated $CpW(CO)_2Me$. A rapid decay (complete in 1 μs) of the entire spectrum to another similar broad spectrum occurs followed by a slow increase in absorbance ($k = 7.2 \times 10^4$ s^{-1}) at ca. 408 nm. Varying the initial concentration of the $CpW(CO)_3Me$ by a factor of 10 (10^{-4}–10^{-3} M) produce no change in this rate constant. Thus the observed reaction cannot be a bimolecular reaction with the starting material, such as oxidative addition to a Cp C–H bond or reactions forming binuclear species.

When THF (0.02–1.0 M) is present in the cyclohexane solution similar behavior is observed. The rate of the initial rapid decay is dependent on the concentration of THF, and in 1 M THF it is nearly complete within 100 ns after the laser flash. The slow increase in absorbance at 408 nm occurs with a rate constant which is independent of the THF concentration (Table I). However, the *magnitude* of this increase in absorbance is inversely dependent on the concentration of THF, that is the greater the THF concentration the smaller the increase in absorbance at 408 nm. This is seen in the linear plot of the final absorbance normalized to the initial absorbance at 408 nm vs. 1/[THF] (Figure 4). We propose the mechanism outlined in Scheme 2 to explain these observations. The initial rapid decay is the trapping of the CO loss product $CpW(CO)_2Me$ by a ligand L which can be either THF or, in the case of no added THF, water[9] to form 3. Water is known to be a good ligand for unsaturated metal centers[10] and

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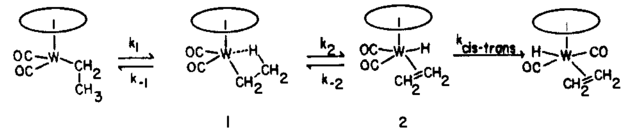
(8) Benson, S. W. *The Foundations of Chemical Kinetics*; McGraw-Hill: New York, 1960.

(9) When dried (by "liquid pumping" see Ref 10a) and water-saturated solutions of $CpW(CO)_3Me$ were photolyzed we were unable to observe differences in the rate of the formation of 3 due to the poor signal-to-noise ratio in the fast time regime. However, the magnitude of the absorbance increase was greater for the dried solution ($A_f/A_i = 1.53$) than for the water-saturated solution ($A_f/A_i = 1.27$) which is indicative that water is participating in the 3 $\rightleftharpoons$ 4 equilibrium in the same capacity as THF does.

Scheme III

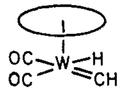


is present in our solutions in 10^{-3} M. The slow increase in absorbance is the reversible process going to **4** with a forward rate constant k_3. We propose that the rate of this step is not limited by loss of L and thus the rate of the forward reaction should have no dependence on [L]. However, since the reverse step is bimolecular and dependent on the ligand concentration the equilibrium concentrations of **3** and **4** should be dependent on [L]. The rate constant k_3 will be dependent on the donor characteristics of L thus a difference in rate for the solutions containing THF and without THF, where L is water, is seen. That k_3 is an order of magnitude greater for L = H_2O vs. L = THF suggests that THF is a better ligand than water for the tungsten complex.

Discussion

The previously proposed model for the photolysis of CpW(CO)$_3$Et is represented in Scheme III.[3a] The cis–trans isomerization step is thought to be rate determining and so steps 1 and 2 are at equilibrium. We have measured the rate constant k_1 for formation of the β-hydrogen solvated structure **1** and derived an activation barrier of 10.8 ± 0.4 kcal/mol for that process assuming a preexponential factor of 10^{13} s^{-1}. The second rate constant measured may be either the rate at which the equilibrium between **1** and *cis*-olefin hydride **2** is set up, i.e., k_2, or if the $\mathbf{1} \rightleftharpoons \mathbf{2}$ equilibrium is fast compared to $k_{\text{cis-trans}}$ then the observed rate constant is $k_{\text{cis-trans}}$. Thus, from our data we can place an upper bound on the activation energy for the β-elimination process to be 12.3 ± 0.4 kcal/mol.

In the photolysis of CpW(CO)$_3$Me the identity of **4** is not known; however, we suggest that it is the product arising from α-elimination (**5**). The *trans*-chromium analogue **6** arising from photolysis of CpCr(CO)$_3$Me has been identified in low-temperature matrices.[11] Such processes have precedence and are proposed to participate in many organometallic reactions.[1,12-16] This process may be expected to exhibit a deuterium isotope effect although none was observed when CpW(CO)$_3$CD$_3$ was photolyzed under identical conditions. Of course the lack of an isotope effect does not rule out the α-elimination product as **4** but further studies are required to firmly establish the identity of this product.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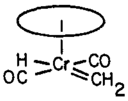
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Registry No. CpW(CO)$_3$Me, 12082-27-8; CpW(CO)$_3$Et, 51232-59-8; CpW(CO)$_2$Me, 73715-35-2; CpW(CO)$_2$Et, 82615-21-2; THF, 109-99-9; H_2O, 7732-18-5.

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Photochemistry of Compounds in the Constrained Medium Cellulose. 7. The Effect of Temperature on Photoinduced Electron Transfer from Tris(2,2-bipyridine)ruthenium(II) to Methylviologen Solubilized in Cellophane

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Abstract: The effect of temperature on photoinduced electron transfer from Ru(bpy)$_3^{2+}$ to MV^{2+} in a cellophane matrix has been studied by steady state and pulsed laser photolysis techniques. The first-order rate constant which depends exponentially on the distance between the reactants shows a non-Arrhenius type of behavior in the temperature interval from 77 to 294 K. This phenomenon, previously found to be of great importance in the biological systems, was quantitatively interpreted in terms of a nonadiabatic multiphonon nonradiative decay process.

The mechanism of electron transfer between reactants, in particular photoinduced electron transfer, is of considerable interest in many avenues of science, both from the point of view of chemists who are concerned with mechanistic features of these reactions and from a biological point of view when the electron transfer between reactants occurs over some considerable distance.[1-9] In

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