Coordination Chemistry Reviews, 111 (1991) 337-343
Elsevier Science Publishers B.V., Amsterdam

The Primary Steps in the Photochemistry of $W(CO)_5L$: Subpicosecond Photochemistry

Cooper H. Langford, Carol Moralejo, Elspeth Lindsay, and D.K.Sharma

Canadian Centre for Picosecond Spectroscopy, Concordia University,
1455 W. deMaisonneuve, Montreal (Que.) Canada H3G 1M8

Abstract

The ligand substitution photochemistry of $[W(CO)_5L]$ (L= py,pip) exhibits higher quantum yields in the singlet region than the triplet region. Across the lowest singlet, yields are higher for ^{1}**E** than ^{1}**A** components. $[W(CO)_5S]$ (S =solvent) forms in less than 20 ps on 355 nm excitation. The primary products observed at 50 ps vary as a function of both leaving group, L, and entering group, S. Solvent effects are consistent with a key role for vibrational relaxation of $[W(CO)_5S]$ on the ground state surface. Heller theory can account for the relative reactivity of triplets, but it is seen that an account of the singlets must exploit more than has yet been brought to bear. Hollebone's octet rule is promising, implying limited utility for Born-Oppenheimer and Franck-Condon Approximations.

Introduction

Consider a bond of bond energy about 300 Kj mol^{-1} and a stretching frequency of less than 500 cm^{-1}, the vibrational period of such a bond is about 1 ps. This hypothetical bond has a shorter vibration period than most metal-ligand bonds. It is interesting to reflect upon how much ligand substitution photochemistry is now known to depend upon primary processes in the picosecond domain or faster (ca. one vibrational period). The number of examples is not inconsiderable. There is evidence that it includes the large number of reactions of approximately octahedral Cr(III) complexes originating from the ^{4}**T** state; the similar, if low yield, reactions of Co(III) complexes from the ^{1}**T** state; and the reactions of d^6 carbonyls following LF excitation. The evidence is a combination of selected picosecond and subpicosecond flash spectroscopy combined with wavelength dependencies of quantum yields that reveal a quantum yield determining step which competes with a ps process.

The Franck-Condon and Born-Oppenheimer approximations may be of limited utility in these cases. Instead, an approach which considers that conservation of momentum involves a coupled response of all constituent electrons and nuclei so that during absorption, the translational and rotational momentum of the photon is converted into internal motions of the molecule - not into its net translation or rotation - may be needed. For this to be possible, the centre of gravity and the axes of symmetry must be unchanged, a condition realized only if all electronuclear accelerations from the photon event are compensated by opposing accelerations in the molecule. This requires that the molecule invoke all internal degrees of freedom in 3D space, requiring a complete description to have 2^3 distinct components - leading to the proposal of an "octupole rule"[1].

Using familiar notation with orbital angular momentum labeled l, spin angular momentum labeled s, and nuclear angular momentum labeled v, we write

$$\Delta L + \Delta S + \Delta V = 3$$

as the selection rule for a transition. Charge transfer bands with electric dipole character will satisfy the rule $\Delta l + \Delta s = 1$. Thus, $\Delta v = 2$ meaning that quadrupolar vibrations maintaining gerade structure and detectable by Raman spectroscopy[2] will accompany electronic excitation. However, there is a low probability of prompt dissociative response because at least two atoms are put into motion to maintain *gerade* structure. In contrast, all three classes of complexes showing prompt dissociation following ligand field excitation have $\Delta v = 1$ or 3 for the LF bands. The response is an asymmetric bond stretch which could readily lead to prompt dissociation.

In this paper, we discuss the emerging evidence for the behaviour of $W(CO)_5L$ (L =pyridine [py], piperidine [pip]) where reactions arise from at least the $^1\mathbf{A}$ and $^1\mathbf{E}$ components in $\mathbf{C}_{4v}$ of the octahedral ^1T state and the lowest $^3\mathbf{E}$ state. Figure 1 indicates the distinct steps in the reactions for which some explicit evidence exists. There are 8 rate constants and 5 states other than the ground state implicated.

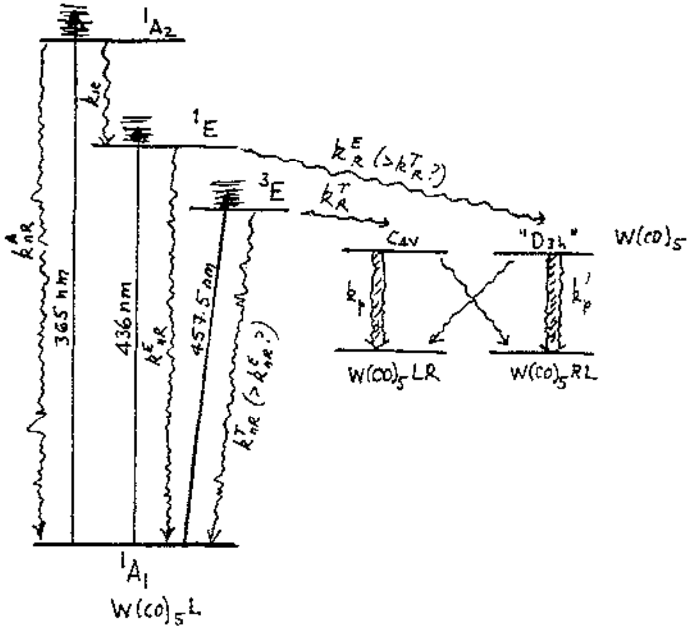

Figure 1. Pathways of reaction of $[W(CO)_5L]$

Results

The purpose of this paper is to draw together a number of features that have been reported in several papers from our laboratory[3,4,5] and others[6,7,8] to achieve an overview. The first important feature is that replacement of L (py, pip) is a wavelength dependent process, with yield increasing toward lower energy in the singlet region from **A** to **E** regions, as first reported by Wrighton[6]. However, continuation to lower energy and excitation of the triplet region reveals reduced quantum yields. Representative results are collected in Table I[3].

Table I

L		Wavelength				
		313^e	365^e	436^e	457.5	488.0
pyr	N_2	$.48(.02)^3$	$.53(.02)^4$	$.62(.02)^4$	$.44(.03)^7$	$.23(.03)^{14}$
	O_2	$.52(.03)^4$	$.54(.02)^{11}$	$.62(.04)^9$	$.44(.03)^7$	$.23(.01)^7$
		.38(.04)	.50(.05)	.63(.06)	(ref 46)	
pip	N_2	-	$.49(.03)^7$	$.54(.02)^2$	$.41(.02)^4$	$.37(.02)^4$
	O_2	-	$.48(.01)^4$	$.53(.02)^3$	$.44(.01)^6$	$.40(.02)^2$

a) concentrations of reactants are between 1.5-6.5 x 10^{-4} M

b) light intensities are between 3 x 10^{-10} and 2 x 10^{-8} Einsteins/sec

c) numbers in parentheses represent standard deviations

d) superscripts represent the number of trials

e) ± 10 nm

The formation of $W(CO)_5$ from the hexacarbonyl appears to occur in less than 500 fs[7,8] and the first observable ground state product, $W(CO)_5S$ (S = solvent, even an alkane) in less than 20 ps[7,8,9]. The formation of $W(CO)_5S$ from $W(CO)_5L$ is even faster[3] (< 10 ps), leaving no reason to assume that dissociation of py or pip is slower than CO loss. It appears that the rate of formation of $W(CO)_5S$ from $W(CO)_5$ is controlled by "slow" vibrational relaxation on the ground state potential surface. This has been established by femtosecond spectra for the Cr analog and provides the only plausible interpretation of the complex pattern of solvent dependence of yields seen in Table II[4]. It is clear that solvent effects are not related to either viscosity, dielectric constant, or donor characteristics. The rough relation to solvent mass supports the theoretically plausible suggestion that vibration-translation energy transfer discriminates among solvents in the highly excited region where the system begins to descend the ground state surface.

Table II. Solvent Dependence of Quantum Yields[a]

solvent	solvent parameters[b]					quantum yield				
						$W(CO)_5$pip		$W(CO)_5$py		
	AN	ε	E_T	Vis	SMW	365 nm	436 nm	313 nm	365 nm	436 nm
CCl_4/1-hexene	2.24	8.6	32.5	0.969	153.82	$0.68\ (0.02)^6$	$0.55\ (0.02)^{14}$	$0.61\ (0.01)^5$	$0.80\ (0.02)^6$	$0.74\ (0.02)^{17}$
1-hexene	2.04				84.16	$0.52\ (0.03)^8$	$0.62\ (0.02)^{12}$		$0.60\ (0.03)^9$	$0.73\ (0.03)^{10}$
isooctane/1-hexene	1.94		32.0	0.390	114.23	$0.49\ (0.03)^{15}$	$0.54\ (0.02)^7$	$0.50\ (0.03)^7$	$0.53\ (0.02)^{13}$	$0.62\ (0.03)^{13}$
$CHCl_3$/1-hexene	4.81	23.1	39.1	0.855	119.38	$0.45\ (0.03)^5$	$0.50\ (0.04)^{17}$	$0.48\ (0.02)^5$	$0.47\ (0.06)^8$	$0.57\ (0.03)^{11}$
C_6H_6/1-hexene	2.28	8.2	34.5	0.912	78.11	$0.42\ (0.02)^4$	$0.45\ (0.02)^{11}$	$0.49\ (0.04)^4$	$0.52\ (0.02)^8$	$0.55\ (0.03)^6$
CH_2Cl_2/1-hexene	9.08	20.4	41.1	0.450	84.93	$0.41\ (0.02)^8$	$0.42\ (0.02)^{11}$	$0.38\ (0.05)^{13}$	$0.44\ (0.04)^5$	$0.54\ (0.01)^6$

[a] Solvents are mixed in a 2:1 v/v ratio with 1-hexene. Standard deviations are given in parentheses. [b] AN = acceptor number,[24] ε = dielectric constant, E_T = local polarity,[25] Vis = viscosity, and SMW = solvent molecular weight. ε, Vis, and SMW values were taken from: *Handbook of Chemistry and Physics*, 64th ed.; CRC Press: Boca Raton, FL, 1984.

After a delay of 50 ps following excitation, $W(CO)_5S$ is essentially fully formed in all cases. However, this is not a single product in all circumstances[5]. Consider the reaction of the pentacarbonyl fragment with 1-hexene. There is a substantial probability, if the reaction is fast enough, that "S" will coordinate *via* an alkyl group as it does in hexane. As well, there is some probability that the alkene function will be directly coordinated. We see evidence at 50 ps for the initial coordination of an alkyl group. The spectrum relaxes to that of the alkene coordinated final stable product with a time constant near 700 ps. Similar phenomena are seen with butanol and octanol where initial coordination of an alkyl group is in evidence at 50 ps, but the final stable product after a few ns is the -OH bound ligand. Analogous phenomena have been seen with Cr carbonyls[10].

If it is assumed that the extinction coefficient of the transient found in hexane and cyclohexane is the same as that for an alkyl coordinated 1-hexene or alcanol, and that the yield for the intermediate in hexane or cyclohexane is the same as the yield for a net product when a good ligand is added to the solution (an L independent yield!), the concentration of the initially formed alkyl product can be calculated since the other extinction coefficients required are all available from stable products. Table III shows the product distribution between alkyl coordination and -OH or >C=C< coordination at a delay of 50 ps following excitation. The results clearly support a difference in selectivity for $W(CO)_5$ generated in different circumstances. Note that the errors introduced by the assumption required will not affect the relative values as the leaving group is changed. The intercomparison of the different solvents for one leaving group is subject to greater uncertainty.

Discussion

The wavelength dependence leads to the suggestion that the fast reactions proceed from at least two different excited states. The lower yield in the triplet region shows clearly that excitation in the singlet region cannot simply be a means of populating a reactive triplet. The lower yield at higher energy in the singlet region minimally implies that relaxation to the ground state competes with crossing to the ^{1}**E** following excitation into the ^{1}**A** region. Figure 1 shows a reactive path from the ^{1}**E** and ^{3}**E** states. We cannot exclude a reaction from ^{1}**A**, but it is not required by the evidence. An important point is that the reaction from the triplet shows a ratio of yield for py loss to pip loss reversed from the singlet, analogous to the change found for Co(III) amines for Cl^- *vs* NH_3 yields. This underlines the distinctiveness of the two reaction pathways.

The justification for the presentation of two distinct $W(CO)_5$ intermediates in Figure 1 (prior to solvent incorporation) comes from the selectivity shown in the products observed at 50 ps. Here, the experiment is limited by the shortage of excitation wavelengths for time resolved spectroscopy. The only wavelength available for exciting these compounds is 355 nm which corresponds to singlet excitation in $W(CO)_5L$ complexes. In the case of $W(CO)_6$, 355 nm excitation is in the triplet region, so it is not clear that we have compared the singlet to triplet behaviour in a single compound. Nevertheless, the percentage of alkyl product formed initially is small when $W(CO)_6$ is irradiated in the triplet, suggesting that a $W(CO)_5$ species forms which can *discriminate* between the poorly coordinating alkyl end of a solvent molecule and the more favourable ligand end, preferring the latter. In contrast, the result with py and pip complexes where excitation is in the singlet region is the formation of a $W(CO)_5$ species which seems to give a more nearly random distribution of alkyl and good ligand products.

The suggested connection between excited states, $W(C))_5$ intermediates, and isomeric $W(CO)_5S$ products (represented RL when an alkyl group coordinates and LR when a stronger donor coordinates) which is shown in Figure 1 is a minimum specification. Each of the arrows shown is required in order to account for the differentiation of paths described above, but other arrows are not excluded. That is, if we require that $^3W(CO)_6$ give the $W(CO)_5$ intermediate which is precursor to a predominately alkyl product, $W(CO)_5RL$, we cannot exclude the formation of some of the other intermediate from the same triplet excited state. Similar comments will clearly apply to other "missing arrows".

Theoretical interpretation

Two major theoretical initiatives exist in the literature which are candidates for use in the interpretation of sub-picosecond photochemistry which is controlled by events rapid compared with thermalization. One is Heller's fourier transform of spectra approach[11], the other is Hollebone's selection rule approach[1].

Heller's initiative remarks that the Fourier transform of a spectral envelope is the time evolution of a wave packet on the new potential surface; the excited surface in the case of absorption, the ground state surface in the case of emission. Tutt and Zink[12] carried out a careful analysis of the absorption and emission profiles associated with the ^3E state of $W(CO)_5L$ (L = py, pip) and used the Heller approach to calculate the equilibrium bond extension in this excited state. They were able to establish that the bond extension is greater for W-L than W-CO and that pip suffers greater extension than py. In conjunction with our recent determination of the crystal structure of the pip compound[13] which makes clear that there are no significant differences in the nature of W-N bonding between the two compounds, these considerations offer a satisfying view of the origin of the greater quantum yield for pip loss as compared to py loss. However, there is a serious limit to the analysis so far. The study required use of both absorption and emission spectra. This means that only the thermally equilibrated triplet is studied. The significance of this limit is immediately apparent when we recall that the order of reactivity is reversed on excitation of the singlet! In order to go further with Heller analysis, more precisely resolved spectra over a broader range will be required. As yet, the approach has not addressed the sub-picosecond processes of interest here.

Hollebone's selection rules can carry us a little further toward the time domain of the results. According to the Hollebone rules, an octahedral d^6 complex has the characteristics;

transition	ΔL	ΔS	ΔV
${}^1T_1(I) \leftarrow {}^1A_1(I)$	0	0	3
${}^3T_1(P) \leftarrow {}^1A_1(I)$	1	1	1

In octahedral symmetry, the requirements of the point group require a t_{1u} vibration of which there are two types shown in Figure 2. The one corresponding to $\Delta V = 1$ is the asymmetric stretch (A). The other with $\Delta V = 3$ is the "buckle" mode of Fig. 2 (B). The asymmetric stretch is expected to lead to dissociation with formation of a square pyramid intermediate. The octet rule would predict this to be the fate of the triplet. The "buckle" mode is susceptible to dissociation with considerable rearrangement and one might anticipate *non-selective* recombination because the metal is highly exposed to surrounding solvent. This is the mode predicted for the singlets.

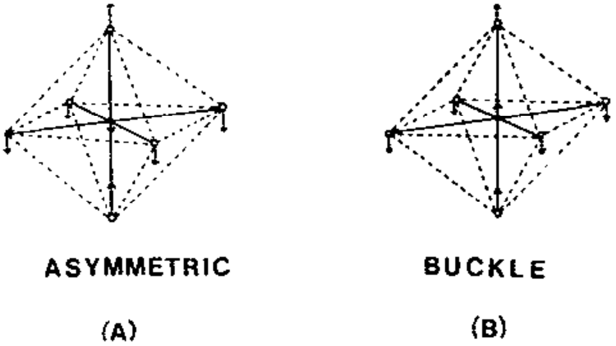

Figure 2. The t_{1u} modes of vibration for $\Delta V = 1$ and 3

The wavelength dependence across the singlet region is accounted for by consideration of the coupling of vibration and electronic quantum numbers in C_{4v}. **E** is the lower electronic component and a rule of overall symmetry conservation[14] requires it to combine with the **A** vibration. This is the vibration weakening the bond to L. In contrast, the upper **A** electronic component must couple with the **E** vibration which corresponds to distortions weakening bonds to the unreactive CO's. Thus, the higher quantum yield in the lower **E** state is predicted.

Similarly, the higher selectivity at 50 ps seen for $[W(CO)_6]$ where reaction originates from the triplet state is explicable on the octet rule. The square pyramid intermediate need only be postulated to be more selective in reactions than the highly distorted "buckle" species with its exposed metal atom. There is some precedent from high time resolution vibrational spectroscopy of intermediates to support the required hypothesis. The indication was that higher symmetry intermediates in analogous Cr systems showed higher selectivity[15].

1.B.R. Hollebone, C.H. Langford, and N. Serpone, Coord. Chem. Revs. 39 (1981) 181.

2.See resonace Raman of CT processes, e.g. D.J. Stufkens, Coord. Chem. Revs. 104 (1990) 39.

3.C. Moralejo, C.H. Langford, and D.K. Sharma, Inorg. Chem. 28 (1989) 2205.

4. C.Moralejo and C.H. Langford, Inorg. Chem. 30 (1991) 567.

5. C. Moralejo, and C.H. Langford, Photochem. Photobiol. A:Chem., 55 (1991) in press.

6. M.S. Wrighton, Inorg. Chem. 13 (1974) 905.

7. M. Lee and C.B. Harris, J. Amer. Chem. Soc. 111 (1989) 8963.

8. A.G. Joly and K.A. Nelson, J. Phys. Chem., 93 (1989) 2876.

9. C.H. Langford, C. Moralejo, and D.K. Sharma, Inorg. Chim. Acta, 126 (1987) 111.

10. E. O'Driscoll and J.D. Simon, J. Amer. Chem. Soc., 112 (1990) 6580.

11. E. Heller, Acct's. Chem. Res. 14 (1981) 368.

12. L. Tutt and J.I. Zink, J. Amer. Chem. Soc. 108 (1986) 5830.

13. C.Moralejo, P.H. Bird, and C.H. Langford, Can. J. Chem. in press.

14. B.R. Hollebone and M.J. Stillman, J. Chem. Soc. Faraday Trans. 2 (1978) 2107.

15. L. Wang, X. Zhu, K.G. Spears, J. Phys. Chem. 93 (1989) 2.

Table III

Primary alkyl product percentages

L	Solvent	450.2 nm
CO	Butanol	3
	Octanol	15
	1-hexene	41
pyr	Butanol	69
	Octanol	100
	1-hexene	48
pip	Butanol	91
	Octanol	115
	1-hexene	80

a) errors are approximately ± 20%