

# Notes

## Wavelength-Dependent Photochemistry of $W(CO)_4(en)$ (en = Ethylenediamine): Evidence for Distinct Chemical Reactivities from Singlet and Triplet Ligand Field Excited States

Rahul S. Panesar, Nicholas Dunwoody, and Alistair J. Lees\*

Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13902-6016

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### Introduction

Studies of the photophysical and photochemical properties of organometallic compounds have now been extensively performed for over 25 years. In considering the photoreactivity of such complexes, it has usually been assumed that their singlet excited states are extremely short-lived and unreactive as a consequence of effective intersystem crossing mechanisms facilitated by the heavy metal and rapid internal conversions to the ground state.<sup>1</sup> For instance, the much studied  $M(CO)_6$  ( $M = Cr, Mo, W$ ) system, which undergoes efficient CO dissociation,<sup>2</sup> appears to conform to this classical model as its determined photochemical quantum yield is independent of the excitation wavelength and all of its substitutional reactivity is attributed to the lowest energy ligand field (LF) triplet state.<sup>3</sup> Also, the *fac*-ClRe(CO)<sub>3</sub>(phen) complex provides an example of a luminescent metal carbonyl system in which metal-to-ligand charge transfer (MLCT) singlet levels undergo intersystem crossing with unity efficiency prior to radiative decay.<sup>1c,4</sup>

Currently, however, experimental evidence is emerging that portrays a more complicated picture of excited-state reactivity in  $M(CO)_6$  and substituted metal carbonyl complexes. One illustration of this is the observation of wavelength-dependence behavior in the photosubstitutional quantum yields of  $W(CO)_5(py)$  and  $W(CO)_5(pip)$  ( $py =$  pyridine;  $pip =$  piperidine).<sup>5</sup> During photochemical investigation of these molecules, it was found that direct irradiation of the lowest lying LF triplet state produced a smaller quantum yield than photolysis of the corresponding LF singlet level, indicating direct reaction from the latter state. Furthermore, studies of picosecond transient absorption spectra, nanosecond transient infrared spectra and photosubstitutional quantum yields in the related  $Cr(CO)_4(bpy)$  ( $bpy = 2,2'$ -bipyridine) and  $W(CO)_5L$  ( $L = 4$ -cyanopyridine

and 4-formylpyridine) systems have led to the conclusion that photodissociation occurs directly from singlet metal-to-ligand charge transfer (<sup>1</sup>MLCT) excited states prior to formation of the corresponding triplet (<sup>3</sup>MLCT) energy levels.<sup>6</sup>

In this paper we report quantitative photochemical measurements obtained for  $W(CO)_4(en)$  (en = ethylenediamine) following excitation into the lowest energy LF absorption manifold at several wavelengths. This system is of particular significance because, unlike most other substituted metal carbonyl complexes, its lowest lying LF absorption band is well removed from other electronic transitions and the lowest energy LF triplet absorption is a distinctive feature of the spectrum. Following excitation at various wavelengths, therefore, it is possible to populate the LF singlet and triplet energy levels exclusively and determine their quantitative photochemical reactivities directly. The results for  $W(CO)_4(en)$  demonstrate conclusively that the LF excited states undergo separate photosubstitutional pathways and that reaction from the lowest lying LF triplet state takes place with a substantially reduced photoefficiency.

### Experimental Section

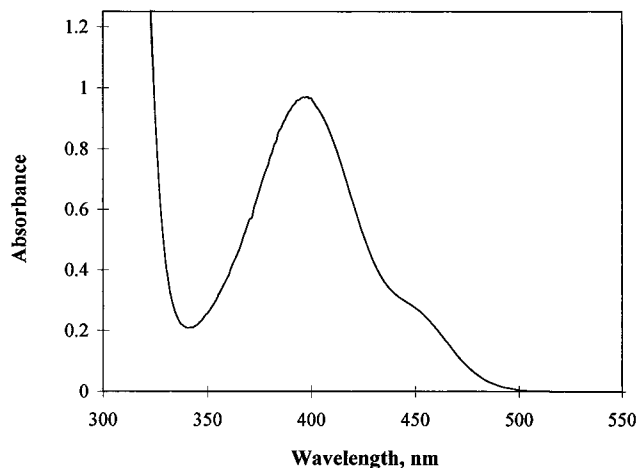
**Synthesis of  $W(CO)_4(en)$ .** The  $W(CO)_4(en)$  complex was prepared by heating 1.76 g of  $W(CO)_6$  and 10 mL of ethylenediamine (en) at 120 °C for 2 h under nitrogen in a modification of a previously described procedure.<sup>7</sup> After heating, 50 mL of distilled water was added to precipitate the yellow complex, which was then collected by vacuum filtration and washed several times with distilled water to remove unreacted en ligand. The crude product was purified by vacuum sublimation to remove unreacted  $W(CO)_6$  and isolated as a bright yellow powder in 47% yield. Purity of  $W(CO)_4(en)$  was confirmed by comparison with literature UV–vis and infrared data. UV–vis,  $W(CO)_4(en)$  in  $CH_3CN$ : 397 nm ( $\epsilon = 1400 M^{-1} cm^{-1}$ ), 450 (sh) nm ( $\epsilon = 400 M^{-1} cm^{-1}$ ) [lit.<sup>8</sup> in  $CH_3OH$ : 397 nm ( $\epsilon = 1400 M^{-1} cm^{-1}$ ), 450 (sh) nm ( $\epsilon = 400 M^{-1} cm^{-1}$ )]. IR,  $W(CO)_4(en)$  in  $CH_3CN$ : 2002 ( $A_1$ ), 1868 ( $B_1$ ), 1851 (sh) ( $A_1$ ) 1807 ( $B_2$ )  $cm^{-1}$  [lit.<sup>7</sup> in  $CH_3NO_2$ : 2006, 1867, 1852 (sh), 1809  $cm^{-1}$ ].

**Photolysis Procedures.** Irradiations at 313, 366, and 405 nm were carried out with light from an Ealing Corp. medium-pressure 200-W mercury arc lamp using interference filters (Ealing Corp., 10-nm band-pass) to isolate the excitation wavelength. Incident light intensities at 313 and 366 nm were determined by Aberchrome 540 actinometry.<sup>9</sup> The incident light intensity at 405 nm was measured by ferrioxalate<sup>10</sup> and Aberchrome 540 actinometry. Photolyses at 458 and 476 nm were performed using the appropriate line from a Lexel Corp. model 95-4 4-W argon ion laser; the incident laser light intensities were calibrated by means of an Ophir Optronics Ltd. model Nova-Display external power meter. Typically, laser powers of 30–35 mW were employed.

In all the photolysis experiments, the solution temperatures were maintained at 293 K. Prior to irradiation, the solutions were stringently filtered through 0.22- $\mu m$  Millipore filters and then deoxygenated by

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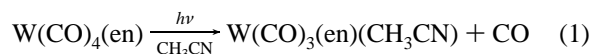
**Figure 1.** Electronic absorption spectrum of  $W(CO)_4(en)$  in acetonitrile at 293 K.

purging with prepurified nitrogen gas<sup>11</sup> for 15 min. Photolysis was carried out on solutions held in regular 1-cm quartz cuvettes; the solution concentrations were typically  $(5-6) \times 10^{-4}$  M. During excitation, the samples were stirred rapidly to ensure homogeneity and a uniform absorbance in the light path. UV-visible spectra were recorded throughout irradiation on a Hewlett-Packard model 8450A diode-array spectrometer. Infrared spectra were recorded on a Nicolet 20SXC Fourier transform infrared spectrometer. Quantum yields were determined by measuring the concentration changes during photolysis over the initial 5–10% of the reaction (where absorbance changes showed linearity with time). Thermal decomposition reactions were monitored simultaneously but were generally found to be negligible over the time period required to perform the excitations. The resultant quantum yield values were determined in triplicate at each excitation wavelength and were found to be reproducible to within  $\pm 10\%$  in all cases.

## Results and Discussion

**Electronic Spectra.** The electronic absorption spectrum of  $W(CO)_4(en)$  in acetonitrile at room temperature is shown in Figure 1. The complex exhibits a band maximum at 397 nm which has been previously assigned to the lowest lying spin-allowed LF transition.<sup>8,12</sup> A low-energy shoulder is also observed at 450 nm; this feature is only revealed by the tungsten derivative and has been attributed to the lowest lying spin-forbidden LF transition.<sup>8,12</sup> In accordance with the LF assignment, these absorption bands are not significantly solvent dependent. Higher energy LF and  $W \rightarrow \pi^*(CO)$  charge transfer transitions are associated with the region immediately below 320 nm.

**Quantum Yields.** Photolysis of  $W(CO)_4(en)$  in deoxygenated room-temperature acetonitrile was performed using excitation wavelengths of 313, 366, 405, 458, and 476 nm. In each case, quantum yields have been determined for the photosubstitution of CO by  $CH_3CN$ , according to eq 1. The measured



quantum yields are shown in Table 1 and illustrate a substantial dependence upon the excitation wavelength. Clearly, photolysis

**Table 1.** Absolute Photochemical Quantum Yields ( $\Phi_{cr}$ ) for the CO Ligand Photosubstitution Reaction of  $W(CO)_4(en)$  in Deoxygenated Acetonitrile at 293 K

excitation wavelength, nm	$\Phi_{cr}$	excitation wavelength, nm	$\Phi_{cr}$
313	0.23	458	0.007
366	0.068	476	0.007
405	0.050		

at 458 and 476 nm into the lowest energy LF triplet region results in significantly reduced photosubstitutional quantum efficiencies compared to the values obtained at 366 or 405 nm involving excitation into the corresponding LF singlet band. On the other hand, the measured quantum yield is even greater following photolysis at 313 nm, upon population of the higher energy LF excited state, indicating that this energy level undergoes CO dissociation via an independent photophysical route with increased efficiency.

The excitation results at 313 and 366 nm for  $W(CO)_4(en)$  are in general agreement with those for other closely related metal tetracarbonyl complexes exhibiting LF excited states. For instance, the photosubstitution quantum yield has been determined to be 0.23 at 366 nm for py loss in  $W(CO)_4(py)_2$  and values ranging from 0.01 to 0.024 have been reported at 313 nm for CO dissociation of a series of  $W(CO)_4(\alpha, \alpha'-diimine) complexes.<sup>12</sup> The quantum yields are somewhat lower for the  $\alpha, \alpha'$ -diimine derivatives, but then the latter complexes possess MLCT transitions lying below the LF manifold. The quantum yield obtained for  $W(CO)_4(en)$  at 405 nm is close to the value at 366 nm, and this is consistent with population of the lowest lying singlet LF state in either case. Importantly, the long-wavelength photochemical data at 458 and 476 nm clearly reveal that directly populating the lowest energy LF triplet level gives rise to much less efficient ligand substitution. Consequently, it can be concluded that the LF singlet state is able to undergo photochemistry directly and more efficiently than the corresponding LF triplet level. The quantum yields demonstrate unequivocally that the singlet and triplet LF excited states each have their own individual reactivities.$

**Excited-State Reactivity.** The quantum yield results for  $W(CO)_4(en)$  reveal a 7-fold reduction when the lowest lying spin-forbidden LF state is populated directly compared to excitation of the corresponding spin-allowed LF level (see Table 1). In contrast, the wavelength dependencies of  $W(CO)_5(py)$  and  $W(CO)_5(pip)$  are considerably lower and the quantum efficiencies are reduced much less (approximately 30–70%) as the excitation wavelength becomes longer.<sup>5</sup> Nonetheless, the data in each case identify a clear difference in the reactivity of the lowest lying LF manifold in these types of complexes. Similar behavior has also been reported for a series of *cis*- $W(CO)_4L_2$  ( $L = py, 4-Me-py, 4-Et-py$ ) complexes with lowest lying LF transitions, although the distinct reactivities of the singlet and triplet states were not specifically addressed.<sup>13</sup>

There may be several contributing reasons for the differing state reactivities in the  $W(CO)_4(en)$  complex. For  $W(CO)_5(py)$  and  $W(CO)_5(pip)$  the reduced triplet reactivity has been rationalized from spectroscopic results on the vibrationally equilibrated LF state which has been shown to undergo substantial excited-state distortion in the form of a “stretch” about the  $W-N$  bond.<sup>5,14</sup> On the other hand, the singlet reactivity has been interpreted using Hollebne’s octapole rule of vibronic cou-

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pling,<sup>15</sup> which associates a "buckle" vibration with this excited state.<sup>5</sup> The increased photoefficiency from the singlet LF state is believed to arise from the fact that in a "buckle" vibration the metal center is exposed to solvating molecules on four octahedral faces. However, additional factors may contribute to the wavelength-dependent behavior in  $W(CO)_4(en)$ . One of these is the possibility of solvent cage effects affecting the singlet and triplet excited LF states in different manners. The spin-forbidden state will obviously be longer lived, and the influence of solvent cage may also be anticipated to be greater; this would tend to enhance ligand-trapping and recombination processes and, hence, increase radiationless deactivation mechanisms relative to ligand dissociations from the triplet level. Another possibility is that the lower lying LF triplet state may be subjected to increased nonradiative relaxation rates through energy gap law effects; this would also serve to reduce the photoefficiency of reaction from this level. More theoretical analysis is needed to understand more about the structure and reactivity of the LF excited states in metal carbonyl complexes such as  $W(CO)_4(en)$ .

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The quantum yield results provide an interesting comparison to those recently obtained for the  $(HBPz'_3)Rh(CO)_2$  ( $Pz' = 3, 5$ -dimethylpyrazolyl) system in which absolute photoefficiencies of C–H bond activation ( $\Phi_{CH}$ ) have been determined to be dependent on the excitation wavelength.<sup>16</sup> It is noticeable that the photophysical properties of this complex appear to parallel those of  $W(CO)_4(en)$  because the  $\Phi_{CH}$  values also reduce significantly as one moves to longer exciting wavelength within a LF absorption band. Similarly, the C–H activation chemistry of  $(HBPz'_3)Rh(CO)_2$  has been understood as arising from two different LF excited states with their own individual reactivities.

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