Photochemical Reactivity of W(CO)$_4$(phen): Evidence for Prompt One-Electron Transfer in Competition with Vibrational Relaxation

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Excitation into either the metal-to-ligand charge-transfer, MLCT, band or the ligand field, LF, band of W(CO)$_4$-(phen) promoted an electron transfer to paraquat, PQ^{2+}. This process was observed spectroscopically by the appearance of the characteristic bands of the well-known radical cation PQ$^{•+}$. Both nanosecond and picosecond flash photolysis were used to further examine the electron-transfer reaction. Excitation of W(CO)$_4$(phen) in the presence of 10 mM PQ^{2+} using a 355 nm, 30 ps pulse revealed the formation of PQ$^{•+}$ within the pulse. This suggests the rate of electron transfer is above diffusion control and that either there must be some preassociation between the reactants prior to excitation or the reaction is mediated by formation of a solvent radical (in a "hot" electron transfer(?)). A 355 nm, 10 ns pulse was also used to excite W(CO)$_4$(phen) in the presence of 10 mM PQ^{2+}. Again, PQ$^{•+}$ was formed promptly and persisted for times on the order of microseconds. Subsequently, competition between back electron transfer ($\tau = 17 \mu$s) and net reaction was observed. The possibility of electron transfer to "inert" halocarbons was also investigated. Picosecond and nanosecond flash photolysis of W(CO)$_4$-(phen) using both 355 and 532 nm excitation in a halogenated solvent, C$_2$Cl$_4$, yielded a spectrum indicative of the prompt formation (<30 ps) of reduced C$_2$Cl$_4$. Available estimates of potentials require this to arise from a hot (not vibrationally relaxed) electron transfer.

Introduction

Over the past two decades, there has been much interest in the photochemical and photophysical behavior of transition-metal complexes which possess low-lying metal-to-ligand charge-transfer, MLCT, states.[1−7] A particularly interesting class of organometallic compounds is the substituted metal carbonyls of group VIA metals due to the presence of multiple luminescence from several closely related MLCT states.[8−10] One compound with particularly interesting behavior is W(CO)$_4$-(phen) (phen = 1,10-phenanthroline). What is intriguing about this complex is the combination of unusual photophysical behavior and photochemical reactivity. Not only does it exhibit dual luminescence,[8,9] but it undergoes substitution of a CO ligand in the presence of a suitable nucleophile via different pathways, depending on the wavelength of excitation. Excitation into the ligand field, LF, band leads primarily to a dissociative

substitution,[11,12] whereas an associative mechanism may operate on MLCT excitation as evidenced by concentration and pressure dependence studies.[6,11,12]

Recent picosecond studies in our laboratory[13,14] have revealed that substitution of CO by a nucleophile such as (*n*-Bu)$_3$P in W(CO)$_4$(phen), whether initiated by LF or MLCT excitation, is a prompt process. Moreover, our observation of a wavelength-dependent quantum yield upon excitation into the MLCT band envelope suggests that the reactive process is competitive with vibrational relaxation.[15] This is in accord with recent studies which have shown that CO loss in the homoleptic carbonyl complexes (where the central metal is Cr, Mo, or W) following LF excitation occurs on the femtosecond time scale.[16−19]

One aspect of the photochemical reactivity of W(CO)$_4$(phen) that has not yet been addressed is that of photoinduced electron transfer. Generally, an excited state of a compound is more energetic than the ground state; hence, the former state has both more oxidizing and more reducing power. Consequently, electron-transfer reactions that are not important thermally may play an important role in a photochemical reaction pathway. For example, it has long been known that complexes such as

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$Ru(bpy)_3^{3+}$ participate in photoinduced electron-transfer processes[20,21] as do some neutral organometallic species.[22] More recently, work from our laboratory has shown that the monometallic compound $Cr(CN-Ph)_6$ undergoes prompt photoinduced electron transfer in nonaqueous solvents.[23] It is therefore not unreasonable to expect that $W(CO)_4(phen)$ may also exhibit redox behavior. To learn whether electron transfer plays a role in the photochemical reactivity of $W(CO)_4(phen)$, we have investigated the electrochemical behavior of this compound in addition to its photochemical reactivity in the presence of selected electron acceptors. Our data will show that the photoreactivity of this complex can involve an electron-transfer pathway in addition to the "usual" substitution pathways,[13] depending upon the potential of the electron acceptor. Forster cycle calculations indicate that electron transfer can occur from "hot" (not vibrationally equilibrated) states. These results have important consequences for the photochemical behavior of this and other related complexes. In particular, some of the literature on the photosubstitution processes may need significant reinterpretation.

Experimental Section

Solvents. Spectrophotometric grade toluene and pyridine were obtained from Aldrich and were used as received. Acetonitrile was obtained either from BDH (ACS grade) or from Aldrich (HPLC grade). The former was distilled over CaH_2 under dry nitrogen prior to use, while the latter was used as received. Reagent grade tetrachloroethylene (Fisher) and THF (BDH) were distilled over P_2O_5 and sodium/benzophenone, respectively, under dry nitrogen prior to use.

Materials. Tri-*n*-butylphosphine, $(n\text{-Bu})_3P$, was purchased from Aldrich and used without further purification. The hexafluorophosphate salt of the 1,1′-dimethyl-4,4′-bipyridinium cation, commonly known as paraquat, PQ^{2+}, was prepared by metathesizing $PQCl_2$ (Aldrich) with NH_4PF_6 (Aldrich). The precipitated $PQ(PF_6)_2$ was collected using suction filtration and washed with a copious amount of water to remove any unreacted materials. The product was air-dried, then placed over P_2O_5, and further dried under dynamic vacuum. Tetraethylammonium hexafluorophosphate, $(C_2H_5)_4N(PF_6)$, was prepared by methathesizing $(C_2H_5)_4NBr$ (Aldrich) with NH_4PF_6 (Aldrich). The precipitated $(C_2H_5)_4N$-(PF_6) was collected by suction filtration and washed thoroughly with water. After the product was allowed to air-dry, it was recrystallized twice from a 3:1 (v/v) mixture of ethanol and acetonitrile and vacuum-dried overnight. $W(CO)_4(phen)$ was synthesized under dry nitrogen on the basis of a literature procedure.[24] The compound was purified by recrystallization twice from a mixture of dichloromethane and hexanes. The UV/vis and IR spectra of $W(CO)_4(phen)$ were found to be in good agreement with those cited in the literature.[8] Elemental analyses required for characterization were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada.

Electrochemistry. Cyclic voltammetry was carried out with a Jaissle IMP 83 potentiostat coupled to an EG&G PARC Model 175 universal programmer and recorded on a BBC Goerz megawatt SE780 *X*−*Y* recorder. A platinum electrode was used as the working electrode. All measurements were made in acetonitrile with 0.1 M $(C_2H_5)_4N(PF_6)$ as a supporting electrolyte. The concentration of $W(CO)_4(phen)$ was 10^{-4} M.

Steady-State Photochemistry. Electron-Transfer Measurements. A medium-pressure xenon arc lamp coupled with an appropriate interference filter was employed for photolysis using 365 and 488 nm excitation. Solutions of $W(CO)_4(phen)$ with concentrations between 10^{-3}

and 10^{-4} M were prepared under dry nitrogen and then transferred to a quartz cuvette ($l = 1.0$ cm). An appropriate amount of electron acceptor was then added to this solution prior to irradiation. The photoreaction was monitored spectrophotometrically using a Hewlett-Packard Model No. 8452A diode array spectrophotometer interfaced with an IBM-PC. All solutions were stirred continuously during the irradiation.

Steady-State Photochemistry. Substitution Quantum Yields. An argon ion laser (Coherent, 4W-all line) was employed for photolysis using 488.0 and 514.5 nm excitation, whereas a dye laser (Coherent CR-590) using Rh-6G was used for irradiation at 610.9 nm. In all cases, a lens was used to expand the beam to the size of the photolysis cell to avoid any complications associated with two-photon processes. Solutions of $W(CO)_4(phen)$ with concentrations between 10^{-4} and 10^{-3} M were prepared under dry nitrogen and then transferred to a quartz cuvette ($l = 1.0$ cm, $V = 3.0$ mL) for irradiation. In all cases, isosbestic points were retained throughout the photolysis, but solutions irradiated to a conversion of less than 10% were used in quantum yield calculations. All solutions were stirred continuously during the irradiation. The photoproduct, $W(CO)_3(phen)(n\text{-Bu}_3P)$, was detected spectrophotometrically. That the product was $W(CO)_3(phen)(n\text{-Bu}_3P)$ was confirmed by comparing the spectral bands observed in the photolysis to those observed from an independently synthesized sample (which was synthesized under dry nitrogen and then purified according to a literature procedure[25]). The light intensity entering the photolysis cell was determined using aberchrome 540P[26] for excitation wavelengths of 488.0 and 514.5 nm. The light intensity entering the photolysis cell when the excitation wavelength was 610.9 nm was determined using aberchrome 999P.[26] The equations described in ref 8 were used to calculate the photochemical quantum yields. The standard deviation for all measurements was less than 10%.

Nanosecond Spectroscopy. Either a Lumonics excimer laser run with argon chloride to give 308 nm pulses (to 80 mJ, 10 ns width) or a Spectra-Physics Nd:YAG laser, frequency doubled or tripled to give 532 or 355 nm pulses (to 50 mJ, 15 ns width), was used for excitation. Transient absorption measurements were made with right angle geometry using a Xe lamp, which could be optionally intensified by pulsing, as the probe beam. A Digichrom computer-controlled monochromator, with appropriate color filters mounted in filter wheels was used to remove scattered light and unwanted orders. Detection was achieved by a Hamamatsu R928 photomultiplier and Tektronik 520A digital oscilloscope. The system was controlled by a Mac IIsi computer program written using Labview 3.0. Solutions of $W(CO)_4(phen)$ used in these experiments were prepared under dry nitrogen and had a ground-state absorbance between 0.3 and 0.5 (in a 7.0×7.0 mm quartz cell) at the excitation wavelength. The solutions were stirred and degassed by a nitrogen flow which was interrupted automatically during the measurement cycle.

Picosecond Spectroscopy. Picosecond time-resolved absorption spectroscopy was carried out with a system of conventional design which is described in detail elsewhere.[27] Picosecond absorption spectra were recorded using either second harmonic (532 nm) or third harmonic (355 nm) Nd:YAG excitation with a pulse width of approximately 30 ps. The pulse energies were 2.5 and 1.5 mJ, respectively. The probe pulse was derived by taking a fraction of the fundamental pulse (1064 nm) and focusing it into a solution of D_3PO_4. This resulted in a superbroadened beam ranging from 425 to 675 nm. A delay line enabled the spectra to be recorded at delays from 0 to 10 ns after the excitation pulse. The change in absorbance relative to the spectra obtained without excitation were recorded using an OMA. The spectra reported are the average of six to nine recordings. Solutions of $W(CO)_4(phen)$ used in these experiments were prepared under dry nitrogen and had a ground-state absorbance between 0.3 and 0.5 (in a 2 mm quartz cuvette) at the excitation wavelength. The solutions were thoroughly mixed between measurements.

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Table 1. Data for Picosecond Flash Photolysis of W(CO)$_4$(phen)^a

	acetonitrile^b		10 mM PQ^{2+} in acetonitrile^b	tetrachloroethylene^d
λ_{ex} (nm)	355	532	355	532
ground-state band maximum (nm)	452 ± 2	452 ± 2	452 ± 5	540 ± 2
bleach minimum (nm)	460 ± 10	460 ± 10	458 ± 10	532 ± 10
HE ESA band maximum (nm)	538 ± 10	560 ± 10	c	e
LE ESA band maximum (nm)	582 ± 10	587 ± 10	c	e
τ (ns) HE ESA	1.1 ± 0.1	0.4 ± 0.1	c	e
τ (ns) LE ESA	0.7 ± 0.1	1.0 ± 0.1	c	e

^{a} All transient absorption spectra were recorded at 295 K. ^{b} The solutions in acetonitrile contained 0.02 M H$_2$O, whereas solutions containing 10 mM PQ^{2+} were dry. ^{c} A single, broad ESA band centered at 580 ± 10 nm was observed. This band persisted for times > 10 ns. ^{d} The tetrachloroethylene solution contained 8% (v/v) CH$_2$Cl$_2$ for solubility. ^{e} No ESA was observed in tetrachloroethylene; hence, no lifetimes could be obtained.

Results and Discussion

Electrochemistry. To understand the role of electron transfer in the reactivity of W(CO)$_4$(phen), it is necessary to first understand the electrochemical behavior of this molecule. The single-sweep cyclic voltammogram of W(CO)$_4$(phen) exhibits a well-defined cathodic wave together with the corresponding anodic wave on the reverse scan. (This is shown in Figure 1S of the Supporting Information.) The voltammogram corresponds to the reduction of W(CO)$_4$(phen):

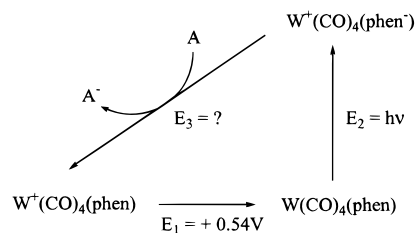$$W(CO)_4(phen) + e^- \rightarrow W(CO)_4(phen)^{\bullet-} \qquad (1)$$

The current, i, observed at the half-wave potential, $E_{1/2}$, is proportional to the square root of the sweep rate. Also, the values of $E_{1/2}$ do not change by more than ±0.01 V for scan rates between 20 and 500 mV/s. This suggests the reduction is a reversible, diffusion-controlled process.[28] The standard electrochemical reduction potential is −1.49 V vs SCE.

Consider now the oxidation of W(CO)$_4$(phen). The single-sweep cyclic voltammogram of the oxidation process is characterized by a cathodic wave showing a well-defined current maximum, but no anodic wave on the reverse scan. (See Figure 2S in the Supporting Information.) The irreversibility of the oxidation is not surprising as the product is a W(I) species which is unstable and will undergo decomposition, providing that the back electron transfer is not prompt.

Examination of the sweep rate dependence reveals that i is independent of the sweep rate as is expected for an irreversible process. However, the $E_{1/2}$ values are independent of the sweep rate, varying no more than ±0.02 V with sweep rates between 5 and 100 mV/s, indicating that the initial electrode processes must be prompt (i.e., the system is not "electrochemically" irreversible).[28] Consequently, the reduction potential for the process can be approximated to be +0.54 V vs SCE using an equation described in ref 27. Such elecrochemical behavior has also been observed in other organometallic systems.[29] Accordingly, it is possible to estimate thermodynamic parameters for electron-transfer processes in W(CO)$_4$(phen) in the presence of a suitable electron donor/acceptor. Corresponding potentials for photochemical processes (excited states) can be estimated using the usual approximations (i.e., Forster cycle).[30] The nature of the electron donor/acceptor and the effect on photoinduced electron-transfer processes involving W(CO)$_4$(phen) will be discussed subsequently.

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Scheme 1

Photoinduced Electron Transfer. Prior to the nature of electron-transfer processes involving W(CO)$_4$(phen) being discussed, it is worth considering the early excited-state behavior of W(CO)$_4$(phen) in neat acetonitrile. Transient absorption spectra of W(CO)$_4$(phen) recorded with 30 ps laser pulses using 355 and 532 nm excitation in neat acetonitrile were reported earlier.[13] Inspection of these spectra reveals three characteristic features. There is a bleach at 460 nm which corresponds to the depletion of the ground state. The bleach forms within the laser pulse and subsequently relaxes back to the ground state. In addition, there are two initial excited-state absorption (ESA) maxima identified by a high-energy (HE) component and a low-energy (LE) component. Both are fully developed in less than 30 ps under both LF (355 nm) and MLCT (532 nm) excitation. These decay on the order of 1 ns. Numerical results are listed in Table 1. These components have been assigned as two closely separated MLCT excited states,[13] describable as W$^+$(CO)$_4$(phen)$^-$, which should be capable of participating in electron-transfer processes, providing that the event occurs prior to the decay of the MLCT excited state.

PQ^{2+} is a well-known electron acceptor which has a reduction potential of −0.45 V vs SCE in acetonitrile solution;[31] hence, under normal conditions, it is unreactive with W(CO)$_4$(phen). However, excited states have better reducing/oxidizing properties than ground states. To learn whether photoinduced electron transfer between W(CO)$_4$(phen) and PQ^{2+} is thermodynamically allowed, a Forster cycle (Scheme 1) can be used to estimate the reduction potential required to oxidize the excited state. Electrochemical measurements show the ground-state oxidation potential to be +0.54 V (see above), whereas the excited-state potential must be approximated using the lowest energy emission band. Previous work by Lees et al. has shown the lowest energy emission band to occur at 771 nm,[8] or 1.6 eV. Therefore, using the Forster cycle shown in Scheme 1, it can be estimated that potentials of −1.1 V (or more, i.e., less negative) are required to convert W$^+$(CO)$_4$(phen)$^-$ to W(CO)$_4$(phen)$^+$. Since PQ^{2+} has a reduction potential of −0.45 V, it can be concluded that photoinduced electron transfer from W(CO)$_4$(phen) to PQ^{2+} is a favorable process.

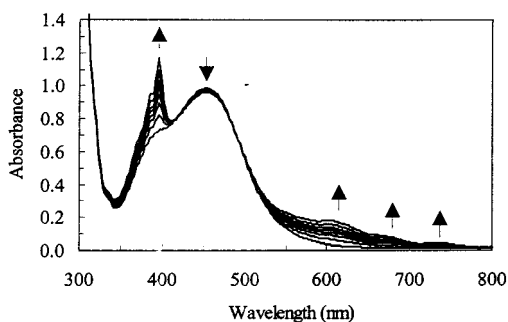(31) Ledwith, A. *Acc. Chem. Res.* **1972**, *5*, 133.

Figure 1. Electronic spectral changes observed upon 488 nm photolysis of $W(CO)_4(phen)$ in a solution of 10^{-4} M PQ^{2+} in CH_3CN over 41 min.
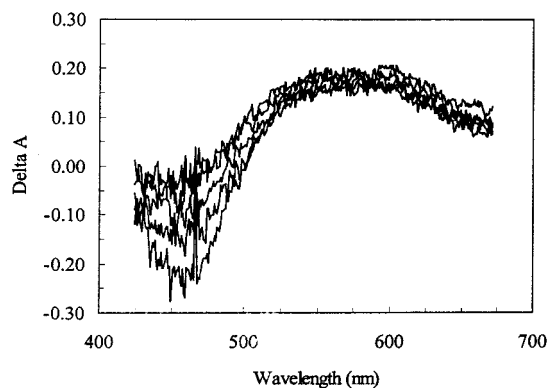

Figure 2. Picosecond absorption spectra of $W(CO)_4(phen)$ in a solution of 10 mM PQ^{2+} in CH_3CN recorded using 355 nm excitation at probe delays of 50 ps, 500 ps, 1 ns, 4 ns, and 10 ns in order of increasing bleach recovery.

Continuous wave excitation at 488 nm in the presence of PQ^{2+} was found to lead to the production of the cation radical $PQ^{\bullet+}$ as evidenced by the appearance of bands in the UV/vis spectrum characteristic of this species.[32] Representative spectra illustrating this reaction are shown in Figure 1. The chemical process can be described as follows:

$$W(CO)_4(phen) \xrightarrow{h\nu} W^+(CO)_4(phen)^- \xrightarrow{PQ^{2+}}_{S}$$
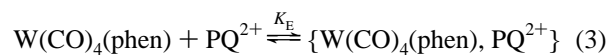$$W(CO)_4(phen)^+ + PQ^{\bullet+} \quad (2)$$
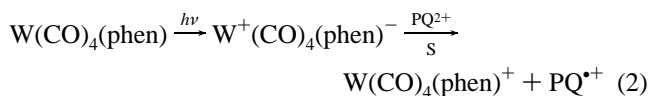
back electron transfer and relaxation

Electron-transfer reactions in other organometallic systems have been shown to occur promptly.[23] Moreover, since the lifetime of the MLCT state of $W(CO)_4(phen)$ is on the order of 1 ns, it is not unreasonable to assume that the electron transfer between $W(CO)_4(phen)$ and PQ^{2+} is fast.

To investigate this possibility, we recorded the transient absorption spectrum of an acetonitrile solution of $W(CO)_4(phen)$ in the presence of 10 mM PQ^{2+} using a 30 ps 355, nm laser pulse. The resulting spectrum, which is clearly different from that observed in the absence of an electron acceptor, is shown in Figure 2. Inspection of the transient absorption spectrum reveals two characteristic features: (1) a bleach at 458 nm which forms within the laser pulse and subsequently decays with increasing time delays (this bleach corresponds to the depletion of the ground state of $W(CO)_4(phen)$), and (2) a reasonably strong transient absorption band centered at 580 nm (this band forms within the laser pulse and persists for times greater than 10 ns). The features of this band are similar to the early time

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behavior of $PQ^{\bullet+}$ as seen in other transient absorption experiments.[33] Thus, $W(CO)_4(phen)$, when excited, promptly transfers an electron to PQ^{2+}. The rate of electron transfer must exceed the diffusion control limit because the reaction between $W(CO)_4$-(phen) and 10 mM PQ^{2+} occurs in less than 30 ps. To explain this high reaction rate, a preassociation of $W(CO)_4(phen)$ and PQ^{2+} prior to excitation must be considered:

$$W(CO)_4(phen) + PQ^{2+} \overset{K_E}{\rightleftharpoons} \{W(CO)_4(phen), PQ^{2+}\} \quad (3)$$

The UV/vis spectra of both $W(CO)_4(phen)$ and PQ^{2+} were recorded separately and compared to the UV/vis spectrum of a mixture of identical concentrations of $W(CO)_4(phen)$ and PQ^{2+} to determine whether there is an encounter complex formed prior to irradiation. The results are summarized in Table 2. Since the mixture has consistently lower absorbance than the sum of the individual components, there is indication of interaction between the components. This is not unreasonable as both $W(CO)_4(phen)$ and PQ^{2+} have large, polarizable aromatic rings and there has been a precedent for interactions between compounds containing such aromatic groups.[34,35] Unfortunately, the observed spectral changes are not large enough to permit quantitative estimation of K_E. (Unfortunately, the key UV/vis spectral regions do not allow for this experiment to be conducted at the same concentrations as used in the electron capture experiments.) However, a minimum value for K_E (3 M^{-1}) was estimated using the Fuoss−Eigen equation[36] It is a minimum because the calculation assumed no interaction between the cationic PQ^{2+} and the polar $W(CO)_4(phen)$, which is unreasonable. Spectral changes no doubt arise from electronic interaction. Using the values for both K_E and the concentration of PQ^{2+}, the fraction of $W(CO)_4(phen)$ in encounter with a PQ^{2+} ion at the time of excitation (and in the first nanosecond thereafter) was estimated to be only 3%. A likely value would be 10 times larger. Nevertheless, this is not sufficient to account for all of the direct electron transfer observed in the picosecond time domain. The only alternative mechanism for the reduction of PQ^{2+} is one in which the solvent, which is 100% in encounter with both $W(CO)_4(phen)$ and PQ^{2+}, acts as the carrier of the electron-transfer process. The solvent radical produced by electron capture from the excited complex is scavenged by PQ^{2+}. Subsequently, we will see this is strongly indicated to be a possibility, despite the requirement that it would be hot electron transfer.

The promptness of the electron transfer suggests it may occur prior to full relaxation of the excited state. This implies the energy of the excited state in the Forster cycle (Scheme 1) could be higher than the 1.6 eV originally estimated from the emission spectrum. Thus, if it is assumed that all of the excitation energy converts the compound from the ground state into the excited state and the electron transfer occurs faster than, or in competition with, vibrational relaxation, the excited-state energy may correspond to as much as the energy of the exciting photons. Consequently, electron transfer can occur to acceptors whose potentials are more negative than −1.1 V. The exact value of the reduction potential will, of course, depend on the excitation

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Table 2. UV/Vis Data for CH$_3$CN Solutions of 1.6×10^{-4} M W(CO)$_4$(phen) and 1.8×10^{-4} M PQ^{2+}

substance	A(262 nm)	A(272 nm)	A(282 nm)	A(292 nm)
W(CO)$_4$(phen)	0.848 72	0.696 93	0.493 13	0.049 10
PQ^{2+}	2.083 4	1.667 1	0.807 62	0.568 65
sum of the bands	2.932 1	2.364 03	1.300 75	0.617 75
W(CO)$_4$(phen) + PQ^{2+}	2.753 5	2.261 4	1.275 6	0.604 93
difference	0.178 6	0.102 63	0.025 15	0.012 82
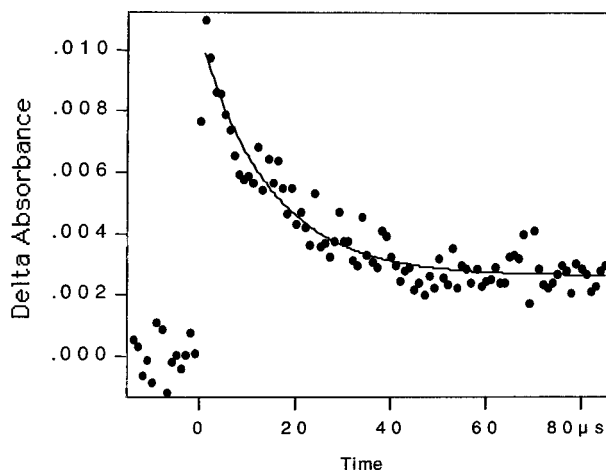
Figure 3. Time trace for the decay of W(CO)$_4$(phen) in a solution of 10 mM PQ^{2+} in CH$_3$CN recorded using 355 nm excitation. The probe wavelength was 610 nm.

Figure 4. Picosecond absorption spectra of W(CO)$_4$(phen) in C$_2$Cl$_4$ (plus 8% CH$_2$Cl$_2$ forsolubility) recorded using 532 nm excitation at probe delays of 50 ps and 5 ns in order of increasing bleach recovery.

wavelength, but certainly can extend to about -2 V. We will return to the consequences of this point later.
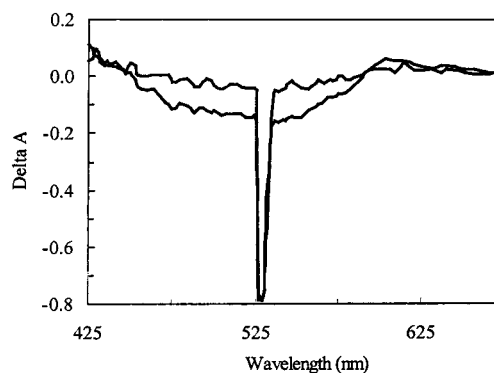
Consider now the back electron transfer that was observed using a nanosecond laser system. With the detector set to monitor at 600 nm (one of the spectral bands of PQ$^{\bullet+}$), a solution of W(CO)$_4$(phen) and PQ^{2+} was irradiated with a 355 nm, 10 ns laser pulse. The decay trace is shown in Figure 3. From this, it is apparent that, within the laser pulse, PQ$^{\bullet+}$ is formed. Its decay was monitored over a period of 80 μs. Analysis of the trace reveals a pseudo-first-order lifetime of 14 μs. It is not surprising that the back electron transfer requires such a long time. Equation 3 shows the electron-transfer products to be cations. Consequently, there will be electrostatic repulsion that may tend to hinder back electron transfer. This rate also indicates that reduction may not occur in encounter where a significant contribution of geminate recombination might be present. Also, W(CO)$_4$(phen)$^+$ may not be stable and may decompose prior to the back-electron-transfer event.

It is interesting that the signal does not return fully to baseline. This indicates a small amount of net photochemistry is happening during the experiment. This can be confirmed with a difference spectrum that corresponds to the spectrum of PQ$^{\bullet+}$. (See Figure 3S in the Supporting Information.)

Returning to the Forster cycle (Scheme 1), if we assign the maximum energy of a 488 nm photon to the excited state, all the energy (2.54 eV) is available to the system. In this case, even a reduction as unfavorable as -2.0 V can drive W(CO)$_4$-(phen) oxidation. This opens a new door for further possible electron-transfer reactivity. For example, the published reduction potential for tetrachloroethylene, C$_2$Cl$_4$, is -1.88 V vs SCE.[37,38]

It therefore appears that electron transfer to this solvent is possible at this excitation wavelength, and for wavelengths up to 532 nm.

The presence of an unusual mechanism is clear upon examination of the picosecond absorption spectrum of W(CO)$_4$-(phen) in C$_2$Cl$_4$ (Figure 4). In this case, there is a marked difference in the early time behavior compared to what was observed in neat acetonitrile[13] and in acetonitrile solutions containing 10 mM PQ^{2+} (Figure 2), or in any of the other solvents reported earlier.[13] It is, however, apparent that absorption of a photon causes excitation of the W(CO)$_4$(phen) molecule as evidenced by the bleach of the ground-state absorption band. A plausible explanation for the behavior in C$_2$Cl$_4$ could therefore be electron transfer from the MLCT state of W(CO)$_4$(phen) to C$_2$Cl$_4$, creating W$^+$(CO)$_4$(phen) and "C$_2$Cl$_4$$^-$". C$_2Cl_4$$^-$ absorbs at 350 nm,[39] so it is not detectable by the picosecond laser system. However, the nanosecond laser system is capable of detection in the UV region. A signal at 350 nm is produced upon excitation of a solution of W(CO)$_4$(phen) at 532 nm in C$_2$Cl$_4$ which decays over a time frame of 1.5 ms (Figure 4S in Supporting Information). This signals the formation of C$_2$Cl$_4$$^-$ upon excitation.

Note that the experiments with tetrachloroethylene were conducted using both 308 and 532 nm excitation to be sure that any observed photoreactivity was solely due to electron transfer between W(CO)$_4$(phen) and C$_2$Cl$_4$, since at the latter wavelength, direct excitation of the halocarbon will not occur (308 nm borders on the "cutoff" for C$_2$Cl$_4$).

Analysis of the decay trace reveals back electron transfer occurs with a lifetime of 750 μs. As in the PQ^{2+} case, the signal does not return to baseline after relaxation, suggesting net photochemistry occurs during the experiment. A difference spectrum does reveal a net bleaching of W(CO)$_4$(phen), indicating decomposition of the starting material. This is not surprising because, as mentioned previously, W(CO)$_4$(phen) $^+$ is not expected to be stable and may tend to decompose prior to the back-electron-transfer event, thereby removing W(CO)$_4$(phen) from the reaction solution. Also, the C$_2$Cl$_4$$^-$ produced as a result

(37) Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in Nonaqueous Systems*; Marcel Dekker: New York, 1970.

(38) The literature value is for a solution of C$_2$Cl$_4$ in a 3:1 dioxane–water mixture–not neat C$_2$Cl$_4$. Since potentials tend to become less negative with decreasing solvent polarity,[35] the actual potental of neat C$_2$Cl$_4$ should be less negative than -1.88 V.

(39) Arai, S.; Tagawa, S.; Imamura, M. *J. Phys. Chem.* **1974**, *78*, 519.

Table 3. Solvent and Wavelength Dependence[a] of the Quantum Yield[b] for the Photochemical Substitution of $W(CO)_4(phen)$ at 298 K upon MLCT Excitation

λ_{ex} (nm)	tetrachloroethylene[c,d]	pyridine	toluene[b]
488	0.0079 (2.1)	0.0028 (4.1)	0.0070 (3.6)
514.5	0.010 (4.4)	0.0027 (3.0)	0.0079 (5.8)
610.9	0.028 (4.0)	e	e

[a] Some nucleophile concentration dependence of yields has been reported.[14] However, the values at 0.3 M of a common nucleophile or in a neat nucleophilic solvent are sufficient to indicate the trends with wavelength in the context of the competition from the electron-transfer pathway under consideration here. [b] The standard deviation (percent) is in parentheses. [c] The reaction mixture contained $(n\text{-}Bu)_3P$ in 0.3 M concentration. [d] 8% (v/v) CH_2Cl_2 was added to the solution to enhance the solubility of $W(CO)_4(phen)$. [e] The quantum yield was not measured in these solvents as the compound did not absorb appreciably at this wavelength.

of electron transfer will not be stable. After the electron transfer, the halocarbon should decompose irreversibly to form Cl^- and chlorocarbon radicals. The chloride ion could thus combine with $W(CO)_4(phen)^+$ with loss of CO to form a chlorinated tungsten complex which should be insoluble in most organic solvents. This was confirmed with the observation of a brown precipitate upon photolysis of THF solution of $W(CO)_4(phen)$ in the presence of C_2Cl_4. Elemental analysis has shown the brown product to contain the following: 8.51% Cl, 36.14% C, 2.81% H, and 5.76% N. Although the exact nature of this product is not yet known, it is reasonable to expect it to be at least bimetallic due to the nature of the excited state (the electron-deficient tungsten fragments will tend to combine to form a stable complex via a Cl bridge). A plausible binuclear formula which fits the analysis reasonably well is $[(phen)(CO)_2W\mu Cl]_2$. Another possibility based on the insolubility of the compound in organic solvents is that the brown species is a Cl-containing polymer of the same stoichiometry. It should be noted that a second set of reaction products is possible for the decomposition of $C_2Cl_4^-$: Cl_2^- and C_2Cl_2.[37] The former species is very oxidizing and will react with virtually everything in the solution. It is therefore apparent that electron transfer to solvent can greatly complicate reactivity.

These points allow for a new interpretation of the reactivity of $W(CO)_4(phen)$. To illustrate the effect of electron transfer to solvent, consider the substitution quantum yields in Table 3. From Scheme 2, it is apparent that the quantum yield for the substitution product should decrease when electron transfer is acting in competition with substitution. This is because the electron-transfer pathway removes the reactive excited state, thereby preventing its reaction with the incoming ligand. In the cases of toluene and pyridine, the wavelength of excitation has little effect upon the substitution quantum yield. This is not surprising, as neither of these solvents can readily accept electrons at these wavelengths. Consider the halogenated solvent C_2Cl_4. If the electron transfer is from a nonvibrationally relaxed excited state, as suggested in the CW experiments with PQ^{2+} and in the time-resolved experiments with both PQ^{2+} and C_2-Cl_4, we can explore the use of excitation energy as "$h\nu$" in the Forster cycle to estimate the potential of $W^+(CO)_4(phen^-)$. Since C_2Cl_4 has a reduction potential of -1.88 V,[37,38] it is apparent that electron transfer can operate for excitation wavelengths up to at least 514 nm. Evidence for a competing electron-transfer

Scheme 2
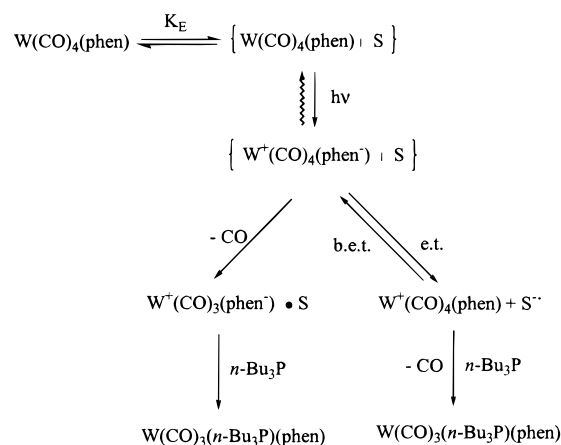
pathway comes from the decreasing substitution quantum yield when the excitation energy is greater than 514 nm. That is, the system can turn the electron-transfer pathway "on" or "off" as a function of excitation energy. The increase of substitution yield under irradiation at 611 nm in C_2Cl_4 is eloquently consistent.

The next most likely solvent to act as an electron acceptor is CH_2Cl_2, where the best available (crude) estimate of the required potential is about -2 V. The observation of transients similar to several other solvents in the picosecond spectra in CH_2Cl_2[13] indicates that electron transfer does not proceed with a 100% yield in CH_2Cl_2.

In conclusion, the data presented in this paper have shown the photochemical reactivity of $W(CO)_4(phen)$ is more complex than what has previously been believed. When the reaction conditions are appropriate, hot electron transfer from a nonvibrationally relaxed excited state of $W(CO)_4(phen)$ occurs; this affects the net outcome. This was seen in the steady-state photolysis measurements when the quantum yield unexpectedly increased with decreasing excitation energy. Consequently, caution must be exercised when a photochemical experiment is designed involving this (or another similar) compound. For example, the reduction potentials of many common "inert" solvents, including acetonitrile and dichloromethane, are in the region of -2 V.[37,38] Accordingly, such solvents may be able to participate in hot electron-transfer processes with an MLCT excited state, thereby producing an unexpected reaction pathway, although we lack definitive evidence at present.

Supporting Information Available: Figures showing single-sweep cyclic voltammograms of electrochemical reduction and oxidation of $W(CO)_4(phen)$, a difference spectrum for $W(CO)_4(phen)$, and a time trace for the decay of $W(CO)_4(phen)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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