Excitation Energy Dependence of Competitive Photosolvation in $W(CO)_5py$

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While competition studies are commonly used in the study of thermal reaction mechanisms,[1] they remain largely unexploited in the study of photochemical reactions despite some telling examples. (1) Kirk and Kneeland monitored the competition between photoaquation and photoanation by NCS^- in $[Co(CN)_5X]^{n-}$ ($X = CN^-$, N_3^-, Cl^-, Br^-, OH^-, H_2O) complexes, also monitoring the ratio of N- and S-bound photoanation products.[2] (2) In studies of photoinduced C−H bond activation in complexes such as $Cp^*Ir(CO)_2$, competition experiments have been used to reveal varying reactivities of hydrocarbons with the active metal complex fragment.[3] Here we report the results of a competition study probing the wavelength dependence of product selection in the photoinduced substitution reaction of $W(CO)_5py$.

The photochemistry of $W(CO)_5L$ (L = pyridine, piperidine) is simple and not complicated by multiple photochemical pathways.[4] The primary photoreaction is the dissociative photosubstitution

$$W(CO)_5L \xrightarrow[S]{h\nu} W(CO)_5S + L \qquad (1)$$

where L is the N-donor ligand and S is the solvent. Picosecond absorption spectroscopy has shown that the primary product $W(CO)_5S$ is formed completely with a time constant of less than 20 ps.[5] Despite the apparent simplicity of this reaction, studies of wavelength and solvent dependence have revealed complicated electronic and medium effects.[5−7] To gain further insight into these effects, photosolvation competition experiments were undertaken.

$W(CO)_5py$ was irradiated in a two-component solvent mixture consisting of equimolar piperidine (pip) and triethylamine (TEA). The reaction mixture was monitored by HPLC at various irradiation times. A sample chromatogram is given in Figure 1. The decrease in $W(CO)_5py$ and the increase in $W(CO)_5pip$ product were quantified. The increase in the product $W(CO)_5TEA$ was not quantified but inferred by difference. Concentrations $[W(CO)_5pip]$ vs $[W(CO)_5py]$ were plotted and the slopes determined over the first 10% conversion in each run. Secondary photoproducts were not detected by HPLC up to 10% conversion and were only observed for conversions greater than 70%. Plots of $[W(CO)_5pip]$ vs $[W(CO)_5py]$ were linear from 0 to 10% conversion, ruling out complications arising from secondary photolysis and differential absorption of the products. Runs were performed in triplicate at four different irradiation wavelengths: 313, 365, 436, and 488 nm. Wavelengths were selected (±20 nm) with interference filters. The irradiation source was a medium-pressure Xe/Hg arc lamp.

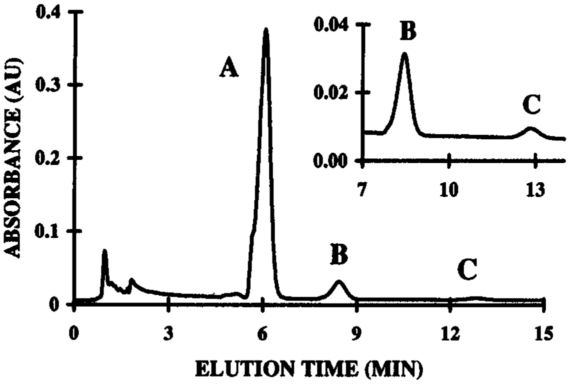

Figure 1. Chromatogram of a 365-nm photolysis mixture. Peaks are (A) $W(CO)_5py$, (B) $W(CO)_5pip$, (C) $W(CO)_5TEA$. The inset shows the product peaks. LC analysis was performed on a C_{18} column, with a tunable absorbance detector set at 310 nm. 60:40 acetonitrile/water was the eluent.

Table 1. Product Ratios with Varying Excitation Wavelengths

excitation energy		$-d[W(CO)_5pip]/d[W(CO)_5py]$[a]	$d[W(CO)_5pip]/d[W(CO)_5TEA]$[b]
nm	cm^{-1}		
313	31950	0.53 ± 0.01	1.1
365	27400	0.61 ± 0.01	1.6
436	22940	0.80 ± 0.01	4.0
488	20490	0.87 ± 0.01	6.7

[a] Average result from three trials, followed by the standard deviation. [b] Derived values in this column were calculated from the experimentally determined ratios $-d[W(CO)_5pip]/d[W(CO)_5py]$.

Results are listed in Table 1. At high excitation energy (313 nm), the pip and TEA-substituted products are formed in a ratio that is close to statistical. As the excitation energy is decreased, there is a marked preponderance of the pip product. A plot of the ratio $d[W(CO)_5pip]/d[W(CO)_5py]$ versus excitation energy is shown in Figure 2, revealing an apparent linear relationship between nucleophile selectivity and excitation energy.

The results are highly complementary to solvent effect data. In a previous study, we investigated solvent effects at each of the excitation wavelengths used here.[7] Solvent effects were dependent on the excitation wavelength. At high excitation energy (313 nm), there is a simple, classical viscosity dependence of the quantum yield. At intermediate energies (365 and 436 nm), there is a complex viscosity and thermal conductivity related solvent dependence. At low energy (488 nm), there is only a weak solvent dependence that cannot be explained by a suitably small solvent parameter set. The solvent dependences originate from cage effects. The classical cage effect, where the solvent cage favors recombination of the geminate pair, correlates with solvent viscosity. The thermal cage effect involves the loss of excess vibrational energy from the photoactive species to the bulk solvent. This cage effect correlates with the thermal conductivity of the solvent.

The role of bound excited states (i.e., states having a well-defined potential well) in $W(CO)_5py$ and their relation to the

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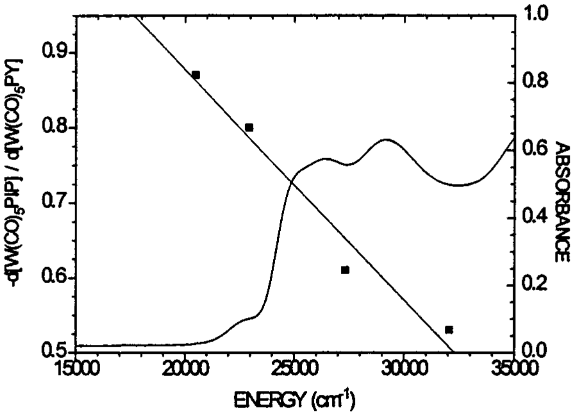

Figure 2. Plot of the slopes $-d[W(CO)_5pip]/d[W(CO)_5py]$ vs excitation energy. The absorption spectrum of $W(CO)_5py$ in piperidine/TEA (1:1, mol:mol) is superimposed (concentration $= 5.7 \times 10^{-4}$ M, measured in a 2 mm quartz cell). The straight line through the data points is the result of a linear regression routine, $r^2 = 0.9725$.

solvent effects observed have been discussed extensively.[7] As excitation energy is decreased, the role of bound states becomes significant as relaxation dynamics permit bound states to trap the system. At high excitation energy, there is sufficient excess energy for the system to overcome the energy barriers to reaction from bound states, and these states play a negligible role in discriminating among multiple relaxation pathways. Solvent effects are closely related to the excited state relaxation dynamics.

The solvent effect data and the competition results presented here illustrate the importance of excess excitation energy in determining the fate of a geminate pair. Excess excitation energy is the difference between the energy contained in the absorbed photon and the ground state bond dissociation energy. This excess excitation energy is distributed as kinetic and vibrational energy in $W(CO)_5$ and py. The loss of kinetic and vibrational energy to the solvent leads to solvent cage effects (i.e., the viscosity and thermal conductivity dependences noted above). The results of this study provide information about the excess vibrational energy of the $W(CO)_5$ fragment and how it affects the reactivity toward donor molecules in the solvent cage. A "cool" $W(CO)_5$ (low excess excitation energy) is quite selective toward nucleophiles. A "hot" $W(CO)_5$ (high excess excitation energy) shows little selectivity. This firmly underlines that products can be determined prior to vibrational relaxation, probably in a non-Born−Oppenheimer domain.

It is interesting to note that significant differences in nucleophile selectivity can be measured in this system. A picosecond absorption study into the nature of the primary products, $W(CO)_5S$, present 50 ps after a 355-nm flash (high excitation energy),[8] shows that long-chain alcohols and alkenes form alkyl-coordinated transients (i.e., σ complexes) in large excess of the alcohol- and alkene-coordinated final products. The stable products are formed in approximately 600 ps. In 1-butanol, 70% of the products at 50 ps were alkyl-coordinated transients. For this competition study, it might then be expected that most of the primary products are σ complexes and that no significant competition for nucleophile donor atoms would occur. If the competition somehow involved σ complexes and not naked $W(CO)_5$, a wavelength-independent ratio of products would be expected. This is not the case.

To our knowledge, this is the first time that a competition study has been used to probe the wavelength dependence of a photochemical reaction. Competitive photosolvation may prove to be a versatile method in mechanistic photochemistry due to the flexibility in the choice of donor solvents that can be used. While this study relied on steric differences between secondary and tertiary amines, it should be possible to exploit electronic differences between solvents with different donor atoms (e.g., phosphines vs amines). Competition experiments on similar photochemical systems are in progress.

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Supporting Information Available: Text describing the experimental procedures and sample plots of $[W(CO)_5pip]$ vs $[W(CO)_5py]$ (3 pages). Ordering information is given on any current masthead page.

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