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The Kinetics of Photodissociation of Tungsten Hexacarbonyl

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Subnanosecond flash photolysis at 355 nm of $W(CO)_6$ in perfluoromethylcyclohexane reveals that the solvatopentacarbonyl intermediate is formed with a first order rate constant of 5×10^{10} s^{-1} at 20 °C. Similar rates are obtained in cyclohexane and a paraffin oil.

The hexacarbonyls of Cr, Mo, and W undergo high quantum yield photosubstitution reactions via a primary intermediate of C_{4v} symmetry, $M(CO)_5S$ where S is a solvent molecule. These species have been well characterized in a variety of media [1], and display a first ligand field (LF) band which, may appear in the visible if the solvent, S, is a sufficiently weak electron donor. If the solvent S allows the first LF band to be detected in the wavelength range 425–650 nm, it becomes possible to monitor the formation of the primary intermediate with the 'continuum' pulse produced in the mode locked Nd/YAG laser system used for flash photolysis with a 20 ps time resolution in the Canadian Centre [2]. Two solvents which permit observation of the intermediate $W(CO)_5S$ with our apparatus are cyclohexane and perfluoromethylcyclohexane. In the first case, the first LF band lies just to the blue of our probe and the tail of the band may be monitored. In the case of the perfluoro solvent, the band is in the visible as has been reported for the analogous $Cr(CO)_5S$ complex [3]. Figure 1 displays the growth of the absorption maximum for the species $W(CO)_5S$ in perfluoromethylcyclohexane in the period between 0 and 100 ps after excitation of a solution 18 mM in $W(CO)_6$ with a pulse of ~2.5 mJ, 30 ps half width, at 355 nm (third harmonic). The rate constant at 20 °C for the growth of the solvopentacarbonyl species is 5×10^{10} s^{-1}. The corresponding rate in cyclohexane is not demonstrably different although the shift of the peak beyond the range of the probe pulse renders quantitative estimation less precise.

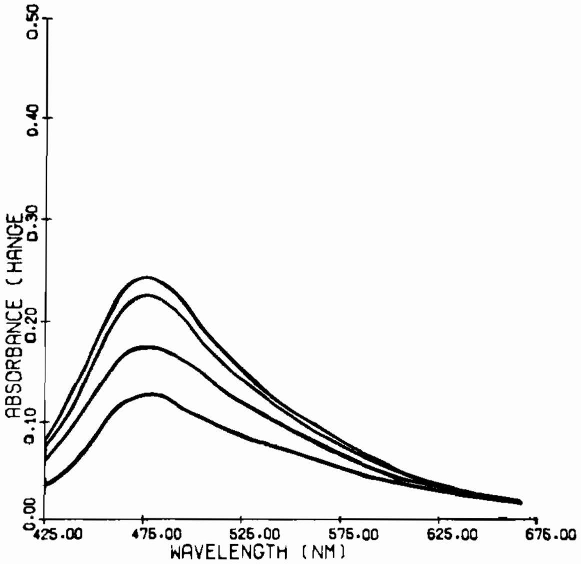

Fig. 1. Growth of absorbance for $W(CO)_5S$ in perfluoromethylcyclohexane. The curves shown reading from bottom to top are spectra at 0, 20, and 50 ps and 1 ns. Each curve is the average from ten pulses. Standard deviation is less than 0.03 A units.

The suggestion has been made [4] that the photodissociation of CO from $W(CO)_6$ occurs from the lowest energy excited state, the 'triplet' LF state in analogy to the well characterized LF photochemistry of the d^6 complexes of Rh(III). If this is correct, it is interesting to compare rates. The reactions of triplets of haloammine Rh(III) complexes in water have rate constants between 10^6 and 10^7 s^{-1} [5]. Recent work from these laboratories suggests that triplets of the corresponding Co(III) complexes react at very similar rates [6]. Thus, the tungsten complex is ~10^4 more reactive than the Rh and Co analogs. The large difference in reactivity raises some question about the assumption of a common pathway, although an intersystem crossing rate in excess of 10^{11} s^{-1} is consistent with results on the Co(III) systems [6].

One question which must be raised is the time required for reorganization of the primary and secondary coordination spheres in order to move the first ligand field band from the position in the ultraviolet corresponding to a hexacarbonyl to the observed position in the visible where a poor donor occupies the sixth coordination position. If the excited state lacked a minimum in the potential surface, it is still possible that development of the observed band could occur with a time constant near 15 ps, reflecting only a time analogous to a rotational correlation time. A test of this 'dynamic' explanation was attempted by preparing a solution of $W(CO)_6$ in a viscous paraffin oil. Time constants were not demonstrably longer than those in cyclohexane. This does not support the reorientation explanation, but it does

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not rule it out either since bulk viscosity may be a very poor guide to the reorganization necessary at the local molecular level.

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