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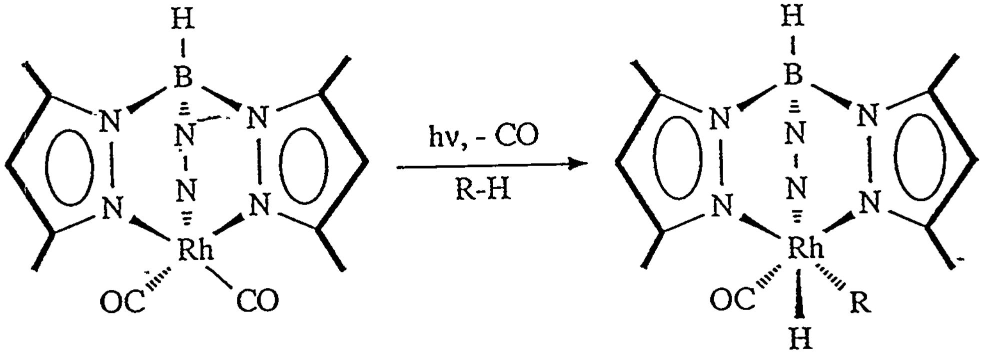
PROGRESS REPORT

Since our last progress report of March 15, 1994 we have devoted much attention to studying the solution photochemistry of $(HBPz^*{}_3)Rh(CO)_2$ (Pz*=3,5-dimethylpyrazolyl) in various hydrocarbons (eq. 1). This metal complex has been reported to C-H activate hydrocarbon substrates readily, even in sunlight.[1] However the mechanism by which it does so is not known, nor is the absolute conversion efficiency of the intermolecular C-H bond activation process. Consequently, we have begun to carry out a detailed investigation of the photochemical reactivity of this system at several different excitation wavelengths and in a variety of hydrocarbon solvents. The temperature dependence of the photochemistry and the nature of the thermal chemistry has also been studied.



(1)

Figures 1-3 illustrate results obtained for the photochemically-induced intermolecular C-H bond activation of $(HBPz^*{}_3)Rh(CO)_2$ in *n*-pentane at room temperature. These spectra have been recorded *in situ* throughout the photoexcitation process using diode-array and FTIR spectroscopic measurement techniques. The photochemistry is exceptionally clean and uncomplicated by thermal and secondary photochemical processes during the course of these light-induced transformations. A kinetic procedure is used to monitor the photochemical reaction from the observed FTIR data (Figures 2 and 3).[2]

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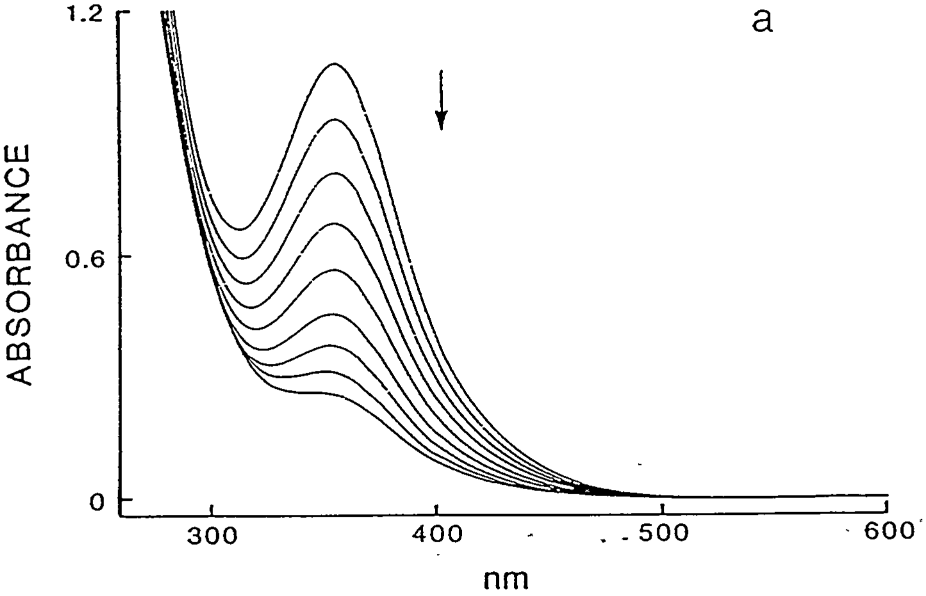

Figure 1. UV-visible absorption spectra accompanying the 366-nm photolysis of 3.4 x 10^{-3} M $(HBPz^*_3)Rh(CO)_2$ in deaerated *n*-pentane at 293 K. Initial spectrum is recorded prior to irradiation; subsequent spectra are depicted following 45 s irradiation time intervals.

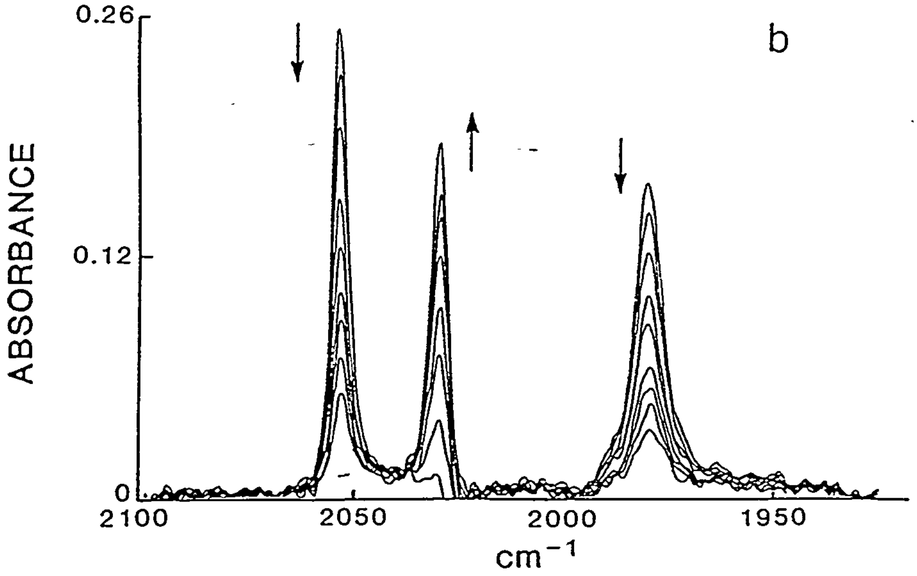

Figure 2. FTIR absorption spectra accompanying the 366-nm photolysis of 3.4 x 10^{-3} M $(HBPz^*_3)Rh(CO)_2$ in deaerated *n*-pentane at 293 K. Initial spectrum is recorded prior to irradiation; subsequent spectra are depicted following 45 s irradiation time intervals.

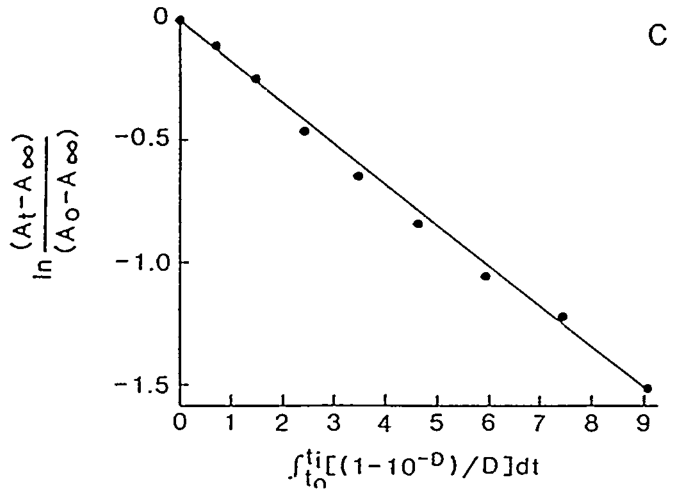

Figure 3. A kinetic representation of the decreasing FTIR absorbance at 2054 cm^{-1} for the photochemical reaction of $(HBPz^*_3)Rh(CO)_2$ in *n*-pentane.

Absolute quantum efficiencies (ϕ_{CH}) have been obtained for the intermolecular C-H bond activation according to an earlier described procedure.[2] The measured values at the various excitation wavelengths are shown in Table 1.[3,4] The ϕ_{CH} data clearly reveal that there is a strong excitation wavelength dependence and that efficient C-H bond activation takes place in the near-UV region. This implies that there are two electronically excited states with different reactivities that are responsible for the overall photochemistry, because the quantum efficiency reduces on photolysis into the long-wavelength tail of the lowest absorption band. These excited states are believed to be ligand field (LF) levels because they have weak absorptivity and show negligible solvent dependence. They also are not luminescent at 77 K, consistent with the LF assignment.[3,4]

Table 1. Absolute Photochemical Quantum Efficiencies (ϕ_{CH}) for the Intermolecular C-H Bond Activation Reaction of $(HBPz^*_3)Rh(CO)_2$ in Deaerated *n*-Pentane at 293 K.

excitation wavelength	ϕ_{CH} [a]
313	0.34
366	0.32
405	0.15
458	0.01

[a] Values were determined in triplicate and were reproducible to within ±5%.

Quantum efficiencies following excitation at 458 nm have been measured at various temperatures: 0.009 (273 K), 0.011 (283 K), 0.011 (293 K) and 0.012 (303 K). The least-squares line of an Arrhenius-type plot of ln ϕ_{CH} versus 1/T yields an apparent activation energy of E_a = 5.4 kJ mol^{-1}, which is too small to invoke thermal activation from the lower LF state to the upper LF level. Furthermore, when the solutions were prior saturated with CO gas (c.a. 9×10^{-3} M) there was no effect on the ϕ_{CH} results at any of the excitation wavelengths. Interestingly, two reaction channels must be occurring; the lower energy state being able to produce a reaction intermediate with a much reduced C-H bond activation reactivity. A (η^2-HBPz*$_3$)Rh(CO)$_2$ species is implicated because the thermal results have revealed that this complex is formed readily it is unable to oxidatively add to RH; hence the long wavelength photochemistry is apparently also dominated by the facile $\eta^2 \rightarrow \eta^3$ back reaction. Contrastingly, the ϕ_{CH} results reveal that the population of an upper excited state leads to highly efficient C-H bond activation. Obviously, the key reaction intermediate produced here is of a very different nature. At these shorter excitation wavelengths, CO extrusion is known to readily take place in metal carbonyl complexes[5,6] and, thus, the photochemical results strongly suggest that the intermediate which is so highly reactive towards hydrocarbon C-H bonds is the monocarbonyl (HBPz*$_3$)Rh(CO) species. The lack of an observable effect of CO concentration on ϕ_{CH} is consistent with an extremely rapid reaction of the photoproduced intermediate with the hydrocarbon substrate.[3,4]

Currently, we are further investigating the nature of the excited states and primary photoproducts in this important C-H activating system. We are also performing an extensive study of the photochemical reactivity in different hydrocarbon solvents, as our early results are revealing that the photoefficiencies in aromatic media are significantly reduced.

In related work we have been studying the emission and electrochemical properties of a series of tungsten(IV) eight-coordinate-chelate complexes containing bidentate picolinato ligands in conjunction with Prof. R. D. Archer at the University of Massachusetts. This is enabling us to characterize environmental effects on the excited state behavior of these metal complexes and to learn more about the photochemical and photophysical pathways from these short-lived electronically excited molecules.

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