Quantitative Photochemistry of (η^5-C_5H_5)Fe(CO)$_2$I in Solution: Effective Heterolytic Fe−I Dissociation upon Long-Wavelength Excitation

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The quantitative photochemistry of (η^5-C_5H_5)Fe(CO)$_2$I in room-temperature solution involving the heterolytic cleavage of iodide to form (η^5-C_5H_5)Fe(CO)$_2$(η^1-*N*-pyrrolyl) has been investigated following irradiation at several wavelengths in the 488−647 nm region. The most effective photoconversions were found to take place with excitation at long wavelengths (580−647 nm) into weak low-lying absorption bands; the absolute quantum efficiency for the photoreaction of (η^5-C_5H_5)Fe(CO)$_2$I in room-temperature toluene has been determined to be 0.38 (±0.02) upon Kr^+ laser photolysis at 647 nm. The photochemical results are in accordance with recent assignments for the HOMO orbitals in (η^5-C_5H_5)Fe(CO)$_2$I and demonstrate that long-wavelength irradiation provides a valuable way of effecting heterolytic Fe−I dissociation, facilitating a synthetic pathway to azaferrocene.

Introduction

Cyclopentadienylmetal carbonyl complexes containing one-electron-donor halide ligands have attracted considerable attention recently as they are known to exhibit a variety of photochemical deactivation pathways. These processes include dissociation of the carbonyl ligand,[1,2] homolytic[3] or heterolytic[4] cleavage of the metal−halide bond, intramolecular isomerization,[1] and intraligand rearrangements.[5] For instance, earlier studies have demonstrated that (η^5-C_5H_5)M(CO)$_3$X complexes (M = Mo, W; X = Cl, Br, I) undergo photochemistry in solutions containing two-electron-donor ligands to yield either ligand-substituted or ionic products via CO and halide ion displacements.[2e,6]

Similarly, in the case of the analogous (η^5-C_5H_5)Fe(CO)$_2$X complex, the primary photochemical process upon 366- or 436-nm irradiation is recognized to involve dissociative loss of a carbonyl ligand.[1] Photolysis of the bromo or iodo derivatives in the presence of triphenylphosphine (PPh$_3$) leads to the formation of the covalent complex (η^5-C_5H_5)Fe(CO)(PPh$_3$)X (X = Br, I) with high quantum efficiency,[1b,c] although it should be noted that (η^5-C_5H_5)Fe(CO)$_2$Cl reacts rapidly with PPh$_3$ in the dark at room temperature to produce a mixture of the covalent (η^5-C_5H_5)Fe(CO)(PPh$_3$)Cl and ionic (η^5-C_5H_5)Fe(CO)$_2$(PPh$_3$)$^+$Cl$^-$ derivatives.[1c] Moreover, photolysis of (η^5-C_5H_5)Fe(CO)$_2$X (X = Cl, Br, I) in benzene solution saturated with ^{13}CO yields (η^5-C_5H_5)Fe(CO)(^{13}CO)X.[1c] Additionally, recent low-temperature work at ca. 12 K following irradiation (λ_{ex} > 300 nm) of (η^5-C_5H_5)M(CO)$_2$Cl complexes (M = Fe, Ru) in methane, nitrogen, and carbon monoxide matrices and in PVC films produced only 16-electron species, confirming that CO dissociation rather than cleavage of the M-Cl bond is the principal reaction pathway.[2d]

In contrast, other studies have revealed that irradiation of (η^5-C_5H_5)Fe(CO)$_2$X can result in the formation of the dimer {[(η^5-C_5H_5)Fe(CO)$_2$]$_2$}, together with Fe^{2+}, X$^-$, and ferrocene, depending on experimental conditions.[3c,4c] Metal−halide heterolysis and metal−metal-bonded dimer formation followed by subsequent disproportionation have been shown to be the main routes for the photochemical formation of ionic products from organometallic halide complexes. In the case of (η^5-C_5H_5)Fe(CO)$_2$I, the reaction involves the initial heterolysis of the Fe−I bond, a step which is recognized as being amine base assisted.[4b]

Although quantitative photochemical measurements have demonstrated that the CO dissociative process in (η^5-C_5H_5)Fe(CO)$_2$X (X = Br, I) proceeds with high quantum efficiency (Φ_{cr} = 0.14−0.89) at 366 or 458 nm,[4b] the optimum excitation wavelength conditions and the photoefficiencies for the corresponding heterolytic Fe−X dissociative reaction are not known. Consequently, we present here a determination of this quantitative photochemistry for the dissociation of I from (η^5-C_5H_5)Fe(CO)$_2$I (see eq 1) following long-wavelength excitation. This reaction was selected for study because it was recently found that the iodide ligand can be replaced by η^1-pyrrole ligands (pyrrole, indole)[7] or imidato ligands (cyclic imides, nucleobases, and nucleosides)[8] in the presence of scavenging diisopropylamine (dipa) base following irradiation with either sunlight or

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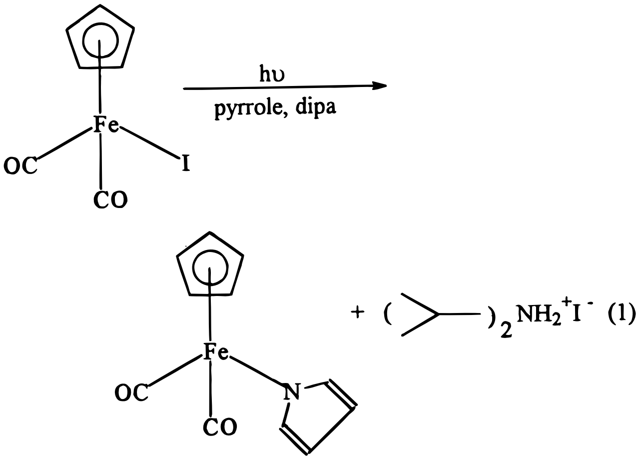

a tungsten lamp. It is important to determine the optimum photochemical conditions for this reaction because the photoproduct, (η^5-C_5H_5)Fe(CO)$_2$(η^1-*N*-pyrrolyl), is valuable as a precursor for the synthesis of azaferrocene.[7b]

Experimental Section

Materials. Cyclopentadienyliron dicarbonyl iodide and pyrrole were purchased from Aldrich Chemical Co. in high purity (97% and 98%, respectively) and used as received. Redistilled diisopropylamine was also obtained from Aldrich Chemical Co. in high purity (97%) and used without further purification. Solvents used in the photoreactivity measurements were purchased from Fisher Scientific Co. and Aldrich Chemical Co. as spectroscopic grade. Toluene was distilled under N_2 from sodium/benzophenone prior to use. Silica gel (200−400 mesh) used in the separation of photochemical products was obtained from Aldrich Chemical Co. Nitrogen gas used for solvent deoxygenation was obtained as high research grade (Union Carbide, >99.99% purity) and was itself deoxygenated and dried by passage over calcium sulfate (W. A. Hammond Co.), phosphorus pentoxide (Aldrich Chemical Co.), and a pelletized copper catalyst (BASF R3-11, Chemical Dynamics Co.) that had been activated with hydrogen gas (Union Carbide, >99% purity) according to a previously described procedure.[9]

Synthesis. The (η^5-C_5H_5)Fe(CO)$_2$(η^1-*N*-pyrrolyl) complex was prepared via photochemical reaction of (η^5-C_5H_5)Fe(CO)$_2$I with pyrrole and diisopropylamine analogous to a previously described procedure.[7b] A solution of (η^5-C_5H_5)Fe(CO)$_2$I (0.7 mmol) in a mixture of toluene (30 mL), diisopropylamine (3.4 mL), and pyrrole (1.1 mL) was irradiated with a 750-W tungsten lamp. This reaction mixture was stirred and cooled by circulating water through a jacketed glass reaction vessel. Immediate precipitation of diisopropylammonium iodide was observed, and the solution gradually turned from black to orange-red. The photoreaction was essentially complete within 1 h, and during this time, the photoconversion was monitored by FTIR spectroscopy. Subsequently, the solution was filtered to remove the amine salt and the filtrate evaporated to yield an orange-red residue, which was chromatographed on silica gel with chloroform as eluent. The product was collected and identified as (η^5-C_5H_5)Fe(CO)$_2$(η^1-*N*-pyrrolyl) in 62% yield. IR in $CHCl_3$: ν(CO) 1996, 1962 cm^{-1} (lit.[7b] in $CHCl_3$: 1995, 1960 cm^{-1}). NMR in $CDCl_3$: δ 6.41 (s, 2H, pyrrolyl α), 6.28 (s, 2H, pyrrolyl β), 5.05 (s, 5H, η^5-C_5H_5) (lit.[7b] in $CDCl_3$: δ 6.36, 6.27, 5.03).

Photochemical Procedures. Visible excitations at 580 nm were performed with light from an Ealing Corp. medium-pressure 200-W mercury lamp and housing apparatus set on an optical rail. A bandpass interference filter (10 nm, Ealing Corp.) was used to isolate the excitation wavelength. Photolyses at 488 and 515 nm were carried out with a Lexel Corp. model 95-4 4-W argon ion laser at various laser powers (30−650 and 20−150 mW, respectively). Excitations at 633 nm were performed with Uniphase model 1105P and Hughes model 3222 H-PC He−Ne lasers with a total laser power of 13 mW. Photolyses at 647 nm were carried out with a Coherent Innova 90 krypton ion laser with laser powers of 11−50 mW. In all laser excitation experiments, the incident light intensities were calibrated by means of an Ophir Optronics Ltd. model Nova-Display external power meter.

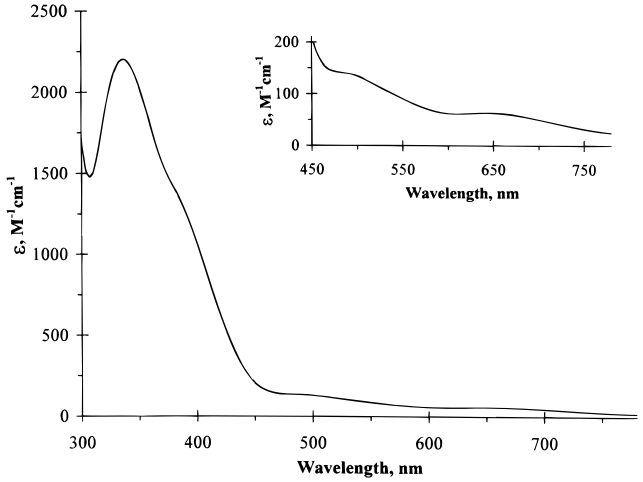

Figure 1. Electronic absorption spectrum of (η^5-C_5H_5)Fe(CO)$_2$I in chloroform at room temperature. The inset depicts weak absorption bands at long wavelength.

During these irradiation experiments, the solution temperatures were controlled to ±0.1 K by circulating a thermostated ethylene glycol−water mixture through a jacketed cell holder. Prior to light excitation the solutions were stringently filtered through 0.22-μm Millipore filters and deoxygenated by purging with prepurified nitrogen gas for 15 min. Throughout photolysis, the solutions were rapidly stirred to ensure sample homogeneity and a uniform absorbance in the light path. UV−visible and FTIR spectra were obtained from solutions at regular time intervals throughout irradiation. Quantum yields for 647-nm excitation were obtained by measuring the concentration changes during photolysis over the initial 50−60% of the reaction and corrected for inner filter effects according to a previously described procedure.[10] Further irradiation was complicated by the precipitation of the photoproduct. The resultant quantum efficiency results were determined in triplicate and were found to be reproducible to within ±5% from the mean value in each case. The iodide substitution reactions were also measured in the dark to assess the extent of thermal processes, and these were determined to be negligible during the course of the photolysis experiments.

UV−visible absorption spectra were obtained on a Hewlett-Packard model 8450A diode-array spectrometer and the reported band maxima are considered accurate to ±2 nm. Infrared spectra were recorded on a Nicolet model 20SXC Fourier transform infrared (FTIR) spectrometer, and the reported band maxima are considered accurate to ±0.5 cm^{-1}. The infrared spectra were typically obtained from solutions using NaCl cells of 0.1−1.0 mm path lengths.

Results and Discussion

Electronic Absorption Spectra. The electronic absorption spectrum of (η^5-C_5H_5)Fe(CO)$_2$I in chloroform at room temperature is dominated by a band centered at 337 nm (ϵ = 2250 M^{-1} cm^{-1}) with a shoulder at ∼ 390 nm (see Figure 1). However, weaker features can also be observed at 486 nm (ϵ = 140 M^{-1} cm^{-1}) and 642 nm (ϵ = 63 M^{-1} cm^{-1}). Although

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Table 1. Electronic Absorption Spectral Data for (η^5-C_5H_5)Fe(CO)$_2$I in Various Room-Temperature Solutions[a]

solvent	λ_{max}, nm (ϵ, $M^{-1}\,cm^{-1}$)
chloroform	337 (2250), 390 (1270),[b] 486 (140), 642 (63)
toluene	344 (2300), 390 (1290),[b] 486 (146), 644 (73)
benzene	343 (2290), 390 (1300),[b] 488 (147), 642 (72)
acetonitrile	330 (2220), 385 (1240),[b] 476 (134), 636 (54)

[a] Reported literature values are 342 (2090) in benzene, 323 (2300) in acetonitrile, and 337 (3010) in methylene chloride (see refs 1b and 4b). [b] Observed as a shoulder.

these bands have not been previously assigned, they are believed to be ligand field (LF) transitions for several reasons. First, the energy positions of these bands have been determined to not be particularly solvent dependent (see Table 1), which is typical behavior of d → d transitions.[11,12] Second, the molar absorptivities of these absorption bands are fairly low, consistent with orbitally forbidden transitions in organometallic complexes.[11] Third, the earlier photochemical studies have demonstrated that these (η^5-C_5H_5)Fe(CO)$_2$X (X = halide) complexes undergo highly efficient CO dissociation following excitation at 366 and 458 nm.[4b]

Photolysis Experiments. Irradiations have been performed at 488, 515, 580, 633, and 647 nm to explore the photochemical processes taking place following excitation into the lowest-energy absorption bands of (η^5-C_5H_5)Fe(CO)$_2$I. In each case, the photochemical transformation of (η^5-C_5H_5)Fe(CO)$_2$I to form (η^5-C_5H_5)Fe(CO)$_2$(η^1-*N*-pyrrolyl) (eq 1) was monitored, under specific experimental conditions where pyrrole (0.6 M) and diisopropylamine (0.6 M) were present in a substantially excess concentration relative to that of the parent complex (5 × 10^{-3} M). The extent of photoconversion was determined by the decline in the carbonyl-stretching vibrations of (η^5-C_5H_5)Fe(CO)$_2$I at 2036 and 1993 cm^{-1} and isolation of the (η^5-C_5H_5)Fe(CO)$_2$(η^1-*N*-pyrrolyl) photoproduct (see Experimental Section). For excitations at 488 and 515 nm, the transformation to Fe(CO)$_2$(η^1-*N*-pyrrolyl) is complicated by CO dissociation reactions, including the formation of the (η^5-C_5H_5)$_2$Fe$_2$(CO)$_3$(η^1-*N*-pyrrolyl) dimer[4b,c] with a characteristic infrared absorbance at 1715 cm^{-1}. Saturation of the solution with CO gas (ca. 1 × 10^{-2} M)[13] was not found to appreciably hinder the CO dissociative process. However, photolyses at 580, 633, and 647 nm were not significantly influenced by CO dissociations and the heterolytic Fe−I cleavage reaction was achieved effectively. A representative photochemical sequence following 647-nm excitation of (η^5-C_5H_5)Fe(CO)$_2$I in toluene is shown in Figure 2, illustrating logarithmic decline of the two infrared bands over approximately 60% of reaction. The spectra did not show such a clean transformation over more prolonged photolysis due to the formation of precipitate. For the same reason the smoothest spectral conversions were observed at low excitation powers (<15 mW).

Quantitative Photochemistry. Absolute photochemical quantum efficiencies (Φ_{cr}) for the heterolytic ligand substitution of I by pyrrole (eq 1) in toluene have been determined following krypton ion laser excitation at 647 nm. Typically, the photochemical reaction was monitored by acquiring UV−vis and FTIR spectra for 50−60% conversion (see Figure 2); on more prolonged photolysis, the spectral data became excessively complicated by precipitation of the iodide salt. The quantum efficiency values (Φ_{cr}) were obtained by application of eq 2,

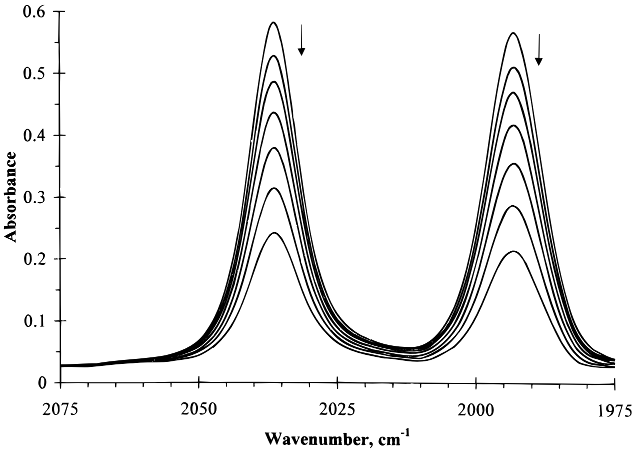

Figure 2. Infrared absorption spectral changes accompanying the 647-nm photolysis of 5 × 10^{-3} M (η^5-C_5H_5)Fe(CO)$_2$I in deoxygenated toluene containing excess pyrrole (0.6 M) and dissopropylamine (0.6 M) at room temperature. The laser excitation power was 11.3 mW. Spectra were obtained following photolysis at 2-min time intervals; the initial spectrum was recorded prior to irradiation.

$$-dC_R/dt = \Phi_{cr} I_0 (1 - 10^{-A_{tot}}) \epsilon_R b C_R / A_{tot} \qquad (2)$$

where C_R is the concentration of the reactant complex at various irradiation times *t*, I_0 is the incident light intensity per unit solution volume (3 mL), *b* is the cell path length (1 cm), and A_{tot} and ϵ_R are the absorbance of the solution and molar absorptivity at the excitation wavelength (ϵ_R is 73 M^{-1} cm^{-1} at 647 nm), respectively. The value A_{tot} constitutes absorbances by both reactant and product complexes at each stage of the reaction; hence, the fraction $\epsilon_R b C_R / A_{tot}$ represents the portion of the absorbed light that is absorbed by the reactant complex in the solution at any particular time. Consequently, eq 2 takes into account the varying inner filter effects caused by the increasing light absorption of the (η^5-C_5H_5)Fe(CO)$_2$(η^1-*N*-pyrrolyl) photoproduct throughout the reaction and it enables quantum efficiency calculations to be performed with a relatively low absorbance at the excitation wavelength.[10] Rearrangement and integration of eq 2 yield eqs 3−5.

$$d \ln C_R = -\Phi_{cr} I_0 \epsilon_R b [(1 - 10^{-A_{tot}})/A_{tot}]\, dt \qquad (3)$$

$$\ln(C_{t_i}/C_{t_0}) = \alpha \int_{t_0}^{t_i} [(1 - 10^{-A_{tot}})/A_{tot}]\, dt \qquad (4)$$

$$\alpha = -\Phi_{cr} I_0 \epsilon_R b \qquad (5)$$

Plots of $\ln[(A_t - A_\infty)/(A_0 - A_\infty)]$ versus $\int_{t_0}^{t_i} [(1 - 10^{-A_{tot}})/A_{tot}]\, dt$, where A_0, A_t, and A_∞ are the infrared absorbances of the ν(CO) bands of (η^5-C_5H_5)Fe(CO)$_2$I throughout the photolysis, were observed to yield straight lines of slope α. The α value has units of reciprocal time, and coincident values were determined following kinetic analysis at either of the ν(CO) bands at 2036 and 1993 cm^{-1}. Moreover, the measured α values were found to be unaffected by variations in the incident light intensity, illustrating that in each experiment the solution was homogeneous and exhibited a uniform absorbance throughout the light path at any point during the irradiation. The quantum efficiency recorded for the 647-nm photolysis of (η^5-

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(13) This value is based on the solubility of CO in *n*-heptane: Lawson, D. D. *Appl. Energy* **1980**, *6*, 241.

$C_5H_5)Fe(CO)_2I$ in 293 K toluene solution is 0.38 (±0.02), based on a mean value of triplicate readings. This quantum efficiency value was also found to be unaffected by the solution temperature in the 283−323 K range.

The relatively high photoreaction efficiency and its negligible temperature dependence are entirely in accordance with the above LF assignment for the long-wavelength absorbance bands in $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$. Interestingly, the experimental results are also consistent with recent MO calculations.[14] For $(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl$, the HOMO orbitals are considered to be a doubly degenerate set of iron−halogen π^* orbitals. Absorption of light thus causes an increase in the Fe−Cl bond order and no heterolytic cleavage is expected. In $(\eta^5\text{-}C_5H_5)Fe(CO)_2I$, however, the HOMO orbitals have been postulated to possess more metal d orbital character and the Fe−I bond order is predicted to decrease; hence, the possibility exists for heterolytic cleavage, as is indeed observed here. Moreover, the long-wavelength photochemistry is of significance as this clearly provides an effective route to new types of $(\eta^5\text{-}C_5H_5)Fe(CO)_2L$ complexes which are, in turn, valuable precursors to azaferrocene. Such synthetic pathways are highly desirable because of the greatly increased reactivity at the metal center of azaferrocene compared to ferrocene.[7b,15]

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