

# Wavelength dependent photochemistry of an iron–arene organometallic photoinitiator: a quantitative study of the photoreactivity†

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The quantitative photochemistry of the widely used cationic photoinitiator complex,  $[\text{CpFe}(\eta^6\text{-isopropylbenzene})]\text{PF}_6$ , has been investigated in several different solvents as a function of exciting wavelength in the 355–683 nm region; the photoefficiency results reveal that the system exhibits a strong wavelength dependence following excitation into its ligand field (LF) manifold and that the photochemistry does not occur solely from the lowest lying LF triplet excited state.

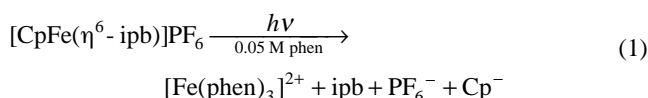
In recent years the  $[\text{CpFe}(\eta^6\text{-arene})]\text{X}$  system (Cp =  $\eta^5\text{-C}_5\text{H}_5$ ; arene = benzene, toluene, hexamethylbenzene, naphthalene, anthracene, pyrene; X =  $\text{BF}_4$ ,  $\text{PF}_6$ ,  $\text{SbF}_6$ ,  $\text{AsF}_6$ ,  $\text{CF}_3\text{SO}_3$ ) has been shown to be an effective cationic photoinitiator in the polymerization of epoxides,<sup>1</sup> dicyanate esters,<sup>2</sup> pyrrole,<sup>3</sup> styrene,<sup>4</sup> dioxolones<sup>5</sup> and acrylates.<sup>4,6</sup> Consequently, complexes such as  $[\text{CpFe}(\eta^6\text{-ipb})]\text{PF}_6$  (ipb = isopropylbenzene) are used widely in industrial polymerization processes, including the manufacture of printed circuit boards<sup>7</sup> and other coating applications.<sup>8</sup> A number of detailed studies of the photochemistry of  $[\text{CpFe}(\eta^6\text{-arene})]\text{X}$  have been carried out and the influence of several parameters (substitution on Cp ligand and nature of arene, counter ion and solvent) on the photoefficiency have revealed that the reactivity involves arene dissociation *via* an initial ring slippage mechanism.<sup>1,9</sup>

Despite the importance of this system our knowledge of the quantitative photochemistry has been restricted. All investigations to date have employed excitation at 436 nm to avoid any light absorption by the entering ligand. At this wavelength the lowest lying ligand field (LF) absorption manifold is populated and it has been assumed that the quantum efficiency for intersystem crossing is unity and that the reactivity occurs exclusively from a lowest energy LF triplet state ( $a^3E_{1g}$ ).<sup>9a</sup> Recently we have developed a photokinetic procedure that enables one to study in detail the wavelength dependence of the photoreactivity in systems where there are inner filter absorbances.<sup>10</sup> Here, we report an investigation of  $[\text{CpFe}(\eta^6\text{-ipb})]\text{PF}_6$  in various solvents; quantitative results have been obtained over a wide range of excitation wavelengths and they clearly show that the photochemistry does not occur solely from the lowest energy triplet excited LF state.

The UV-visible absorption spectrum of  $[\text{CpFe}(\eta^6\text{-ipb})]\text{PF}_6$  in dichloromethane is shown in Fig. 1a and irradiations have been performed at 355, 458, 488, 514, 632 and 683 nm. Excitation in the 458–514 nm region results in population of the lowest lying LF singlet band ( $a^1E_{1g}$ ).<sup>9</sup> Excitation at 355 nm results in population of an upper lying LF singlet band ( $^1E_{2g}$ ) and may also involve some absorption into the long-wavelength tail of a higher lying ligand-to-metal charge transfer (LMCT) transition.<sup>9,11</sup> Excitation at 632 and 683 nm directly populates the LF triplet excited state of the complex ( $a^3E_{1g}$ ),<sup>9a</sup> notwithstanding the extremely low absorbance in this region (in acetone,  $\lambda_{\text{max}} = 650$  nm,  $\epsilon = 3.2 \text{ M}^{-1} \text{ cm}^{-1}$ ).

Fig. 1b illustrates UV-visible absorption spectra that have been recorded during the 458 nm photolysis of  $[\text{CpFe}(\eta^6\text{-ipb})]\text{PF}_6$  in deoxygenated acetone containing 0.05 M phen at 293 K. Spectra are depicted following 1 min time intervals; initial spectrum was recorded prior to irradiation.

ipb)] $\text{PF}_6$  in deoxygenated acetone solution containing an excess concentration (0.05 M) of scavenging phen (phen = 1,10-phenanthroline) ligand. Photolysis experiments have been performed at 355 and 683 nm with a Nd:YAG laser (the latter excitation wavelength utilized a Raman shift of the laser line), at 458, 488 and 514 nm with an  $\text{Ar}^+$  laser and at 632 nm with a He–Ne laser. The spectral sequence depicted in Fig. 1b is representative of those obtained at any of the excitation wavelengths studied and in each case the reaction involves an exceptionally clean conversion to the  $[\text{Fe}(\text{phen})_3]^{2+}$  photoproduct ( $\lambda_{\text{max}} = 510$  nm), according to eqn. (1).<sup>9a</sup> It was determined that the photochemistry was uncomplicated by any thermal processes or secondary photoreactions under these experimental conditions.



Absolute photochemical quantum efficiencies ( $\phi_{\text{cr}}$ ) have been obtained for the arene dissociation reaction of  $[\text{CpFe}(\eta^6\text{-ipb})]\text{PF}_6$  in deoxygenated acetone containing 0.05 M phen at 293 K. Spectra are depicted following 1 min time intervals; initial spectrum was recorded prior to irradiation.

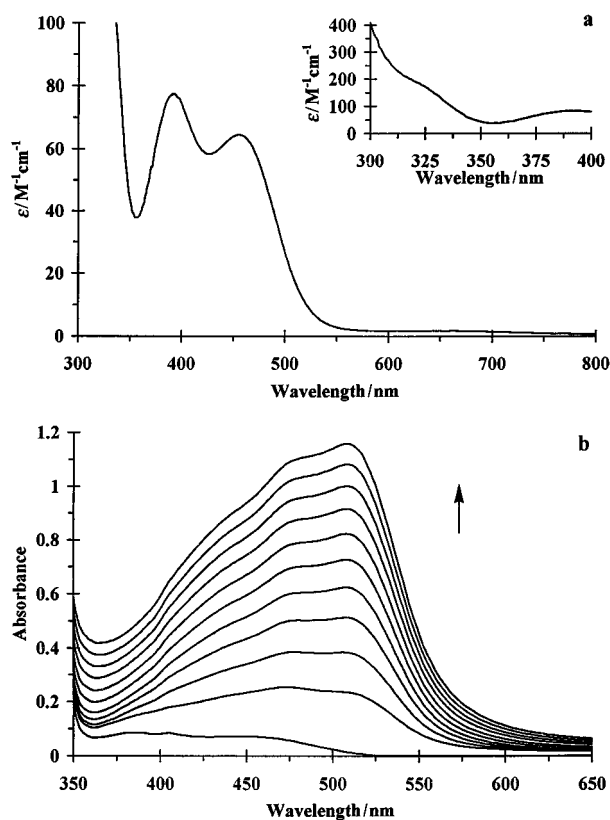


Fig. 1 (a) UV-visible absorption spectra of  $[\text{CpFe}(\eta^6\text{-ipb})]\text{PF}_6$  in dichloromethane at 293 K. (b) UV-visible absorption spectral changes accompanying the 458 nm photolysis of  $1 \times 10^{-3} \text{ M}$   $[\text{CpFe}(\eta^6\text{-ipb})]\text{PF}_6$  in deoxygenated acetone containing 0.05 M phen at 293 K. Spectra are depicted following 1 min time intervals; initial spectrum was recorded prior to irradiation.

† Dedicated to the memory of Dr Stephen J. Fuerniss who died suddenly on October 31, 1998.

**Table 1** Absolute photochemical quantum efficiencies ( $\phi_{cr}$ ) for the arene dissociation reaction of [CpFe( $\eta^6$ -ipb)]PF<sub>6</sub> in various solutions following excitation at several wavelengths<sup>a,b</sup>

Solvent	$\phi_{cr}$					
	355 nm	458 nm	488 nm	514 nm	632 nm	683 nm
Dichloromethane	0.33(0.02)	0.25(0.001)	0.29(0.003)	0.20(0.003)		0.066(0.002)
Acetonitrile	0.66(0.07)	0.64(0.01)	0.62(0.01)	0.49(0.007)	0.20(0.01)	0.15(0.002)
Acetone	0.61(0.03)	0.66(0.01)	0.65(0.01)	0.49(0.008)		0.14(0.004)
Nitromethane	— <sup>c</sup>	0.72(0.01)	0.72(0.006)	0.55(0.003)		0.17(0.002)
1,2-Dichloroethane	0.25(0.02)	0.21(0.001)	0.22(0.002)	0.17(0.002)		0.051(0.002)

<sup>a</sup> Errors estimated at  $\pm 5\%$ ; values in parentheses represent the standard deviations from at least five measurements. <sup>b</sup> phen Concentration is 0.05 M in each case. <sup>c</sup> Value was not obtained due to solvent absorption.

ipb)]PF<sub>6</sub> following excitation at each of the above irradiation wavelengths. These values were determined by our previously reported procedure which accounts for inner filter effect absorbances due to the entering ligand.<sup>10</sup> Such a method is much more accurate than the procedure used earlier (in which  $\phi_{cr}$  values were obtained over a small percentage of reaction<sup>9c</sup>) and it has also facilitated measurement of  $\phi_{cr}$  data at both short and long excitation wavelengths. When phen is present in excess concentration it is understood to act solely as a scavenging ligand and not affect the reaction kinetics.<sup>9c</sup> For each excitation wavelength, the predicted linearity of the data, according to the photokinetic procedure,<sup>10</sup> was indeed observed in plots of  $\ln[(A_t - A_\infty)/(A_0 - A_\infty)]$  versus  $\int_0^t [(1 - 10^{-A_{tot}})/A_{tot}] dt$ , where  $A_0$ ,  $A_t$  and  $A_\infty$  are the absorbance values of the photoproduct at 510 nm during the irradiation, and  $A_{tot}$  is the total absorbance at various irradiation times  $t$ . This confirms that there is only one light step in the photochemistry. Time-resolved absorption spectra obtained for this system have also indicated that the initial photochemistry is extremely rapid (picosecond timescale) and that subsequent ligand scavenging is a much slower dark process ( $k_{bimol} \approx 10^5\text{--}10^8 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>1,9b</sup>

The determined absolute photochemical quantum efficiencies for the arene dissociation reaction of [CpFe( $\eta^6$ -ipb)]PF<sub>6</sub> are shown in Table 1. In each case, the phen concentration was kept constant and in excess (0.05 M) in order to make a fair comparison across all of the excitation wavelengths. The  $\phi_{cr}$  results reveal strong dependence on the exciting wavelength for each solvent studied. The arene dissociation reaction clearly proceeds very efficiently following excitation in the 355–514 nm region into either of the two lowest lying LF singlet states, whereas this process is much less effective upon long-wavelength excitation in the 632–683 nm region following direct population of the LF triplet state. The observed wavelength dependence of  $\phi_{cr}$  demonstrates unequivocally that the reaction does not occur solely from the lowest energy triplet level. If the quantum efficiency for intersystem crossing from the lowest lying singlet excited state ( $a^1E_{1g}$ ) to the triplet reactive state ( $a^3E_{1g}$ ) was unity<sup>9a</sup> then the determined  $\phi_{cr}$  values would represent the processes from the lowest energy triplet state and would be independent of excitation wavelength. One possibility is that in the [CpFe( $\eta^6$ -ipb)]PF<sub>6</sub> complex the lowest lying singlet ( $a^1E_{1g}$ ) and triplet ( $a^3E_{1g}$ ) LF states have distinct photoreactive pathways. Recently, independent photochemical routes occurring from lowest energy singlet and triplet excited states have been identified in W(CO)<sub>5</sub>(py) and W(CO)<sub>5</sub>(pip) (py = pyridine, pip = piperidine),<sup>12</sup> W(CO)<sub>4</sub>(en) (en = ethylenediamine)<sup>13</sup> and CpMn(CO)<sub>3</sub>.<sup>14</sup> Another possibility is that the photoreactivity arises exclusively from the singlet level ( $a^1E_{1g}$ ) and the long wavelength photochemistry proceeds via thermal activation from the triplet ( $a^3E_{1g}$ ) state.

Additionally, the  $\phi_{cr}$  results in Table 1 show a significant solvent dependence for each excitation wavelength with higher  $\phi_{cr}$  values being obtained in more polar solvents. The lower  $\phi_{cr}$  values in solvents with low relative permittivities are understood to be caused by ion-pair formation of [CpFe( $\eta^6$ -ipb)]<sup>+</sup>PF<sub>6</sub><sup>−</sup> and the subsequent participation of the counter ion in the photochemical mechanism. Previously, time-resolved experi-

ments have indicated that the close interaction of the counter ion results in a separate pathway involving a longer lived ring slipped ( $\eta^4$ -arene) reaction intermediate.<sup>9b,c</sup> Such long lived intermediates give additional opportunity for the arene ligand to undergo a reverse ring slippage ( $\eta^4 \rightarrow \eta^6$ ), thereby lowering the  $\phi_{cr}$  values. Currently, a number of solvent effects on the photochemical mechanism are under further investigation.

This study represents the first one in which the photochemistry of the [CpFe( $\eta^6$ -arene)]X system has been investigated quantitatively at different excitation wavelengths. The results illustrate that the photoreaction is extremely efficient in the UV and visible regions, particularly if polar solvents are employed. Moreover, it is noteworthy that the photochemistry can be effectively performed throughout the visible spectrum making it possible to use a variety of laser excitation sources; indeed, the triplet state can be populated directly at 683 nm. The wavelength dependence of the photochemistry reveals that the reactivity does not solely derive from the lowest triplet state, as previously assumed. The strong wavelength dependence in this system will certainly have a major influence on future photoinitiator applications in coatings and moldings, in holography and lithography, in the manufacture of liquid-crystal display devices and protective films for optical devices, and in dentistry.<sup>1–8</sup>

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## Notes and references

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