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A Photophysical Study of Sensitization-Initiated Electron Transfer: Insights into the Mechanism of Photoredox Activity

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Abstract: The development of photocatalytic reactions has provided many novel opportunities to expand the scope of synthetic organic chemistry. In parallel with progress towards uncovering new reactivity, there is consensus that efforts focused on providing detailed mechanistic insight in order to uncover underlying excited-state reactions are essential to maximise formation of desired products. With this in mind, we have investigated the recently reported Sensitization-Initiated Electron Transfer (SenI-ET) reaction for C-H arylation of activated aryl halides. Using a variety of techniques, and in particular nanosecond transient absorption spectroscopy, we are able to distinguish several characteristic signals from the excited state species involved in the reaction, and subsequent kinetic analysis under various conditions has facilitated a detailed insight into the likely reaction mechanism.

With the advent of transition metal photoredox catalysis, many organic reactions previously considered to be unfeasible, due to high activation energies or poorly activated substrates, can now be proposed as viable synthetic pathways.[1] Inspired by photosynthetic reaction mechanisms, where light harvesting and subsequent redox reactions are decoupled, the König group recently reported^[2] conditions for highly efficient C-H arylation of activated aryl bromides, as shown in Scheme 1. In this reaction, C-C bond formation under mild conditions was achieved by exploiting two different components to absorb light and then undertake subsequent redox reactions. Specifically, by using [Ru(bpy)₃]²⁺ as a strong visible light harvesting unit in the presence of a polycyclic aromatic hydrocarbon (PAH) such as pyrene, with the addition of Hünig's base (DIPEA) as an electron donor, formation of the highly reactive pyrene radical anion (Pyr-) was proposed. Upon one electron reduction, subsequent fragmentation of the aryl halide yields the (hetero)aryl radical, which can combine with a trapping reagent such as *N*-methylpyrrole to yield the product after oxidation.

Moreover, since the available reducing power of the pyrene radical anion (-2.1 V vs SCE) is significantly greater than that of the *[Ru(bpy)₃]²⁺ (³MLCT) excited state oxidation potential (-0.81 V vs SCE) and the one electron reduced [Ru(bpy)₃]⁺ complex (-1.33 V vs SCE), the reaction of less reactive aryl halides was also facilitated. This allowed the synthetic scope of this reaction to be expanded to include a variety of aryl chlorides (and pseudohalides) which were similarly activated towards carbon–carbon (and carbon–heteroatom) bond-forming reactions.

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Supporting information for this article is given via a link at the end of the document.

In the reported catalytic cycle,^[2] a key feature proposed was a single electron transfer (SET) reaction from DIPEA to the excited



Scheme 1. Catalytic C-H arylation of an activated aryl bromide in the presence of $[Ru(bpy)_3]^{2+}$ and pyrene as light harvesting and redox active components.

PAH acceptor, ostensibly in its triplet state, Pyr (T_1). Shortly afterwards, some uncertainty in this mechanism was noted,^[3] since the reaction between these two components;

*Pyr (T₁) + DIPEA
$$\rightarrow$$
 Pyr⁻ + DIPEA⁺

should be highly endergonic (*ca.* -1.0 V vs SCE). As a possible alternative, a mechanism involving Triplet-Triplet Annihilation (TTA) to form an excited singlet state, Pyr (S_1), was proposed,^[3] for which subsequent SET to form the radical anion;

*Pyr (S₁) + DIPEA
$$\rightarrow$$
 Pyr⁻ + DIPEA⁺

is more thermodynamically reasonable (*ca.* +2.1 V *vs* SCE).^[3] It was also suggested that direct observation of the radical anion using time resolved absorption spectroscopy, as well as its power and/or concentration dependence, may yield further insight into the reaction mechanism.

Inspired by these reports, herein we discuss our investigation of this reaction using nanosecond transient absorption spectroscopy (ns-TA). This technique has been recognised^[4] as being useful for the identification of important reaction intermediates.^[5] In particular, the $[Ru(bpy)_3]^{2+}$ complex has distinct and easily recognizable ns-TA features. For example, in addition to the ground state bleach (GSB) signal centered at around 450 nm, the ³MLCT excited state of this complex, which is rapidly formed (<100 fs) after photoexcitation, has an additional excited state absorption (ESA) signal in the visible region at ca. 370 and >500 nm, corresponding to newly formed ligand localized (bpy radical) and charge transfer (LMCT) absorption bands.^[6] Similarly, the excited state singlet *Pyr (S_1), triplet state *Pyr (T_1), and radical anion (Pyr-) of the pyrene chromophore have well-known and characteristic ESA features at ca. 470, 520 and 495 nm respectively.^[7]

The reaction conditions initially reported by König could not be used for the purposes of the current study, as this would yield solutions too optically dense for ns-TA analysis. As a result, it was necessary to first benchmark the observed organic reactivity upon 10-fold dilution of the reaction components, which we have undertaken using ¹H NMR and GC-MS analysis. The corresponding reaction conditions and characterisation data are given in the Supporting Information (see Experimental Details and

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Fig. S1 and S2), which showed the desired reaction product is formed, albeit in a lower yield of *ca*. 55 %. These results provide confidence that our spectroscopic measurements are applicable to the catalytic reaction.

Having confirmed the SenI-ET reaction was productive under our diluted reaction conditions, we next sought to investigate the kinetic behavior of the various photogenerated species likely to be present using ns-TA spectroscopy, by employing differing initial concentrations of pyrene and DIPEA. As a starting point, the ns-TA spectra of [Ru(bpy)₃]²⁺ measured in degassed DMSO were collected (see Fig. S3, Supp. Info.), yielding features described earlier corresponding to the GSB and ESA signals of the ³MLCT excited state. Global analysis of this data yielded a monoexponential lifetime of 1.04 ± 0.01 µsec.

Measurements in the presence of differing initial concentrations of pyrene (see Fig. S4-S6, Supp. Info.) revealed quenching of the *[Ru(bpy)₃]²⁺ (³MLCT) excited state lifetime as expected (see Table 1, entries 2-4). This allowed the dynamic Stern-Volmer quenching constant (K_{sv}) for the intramolecular reaction between the *[Ru(bpy)₃]²⁺ (³MLCT) excited state and pyrene to be established (see Fig. S7, Supp. Info.), yielding a bimolecular quenching rate constant for Triplet-Triplet-Energy-Transfer (TTET) of $k_{TTET} = 3.09 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ Also evident in the ns-TA data was the slow appearance of ESA signals at *ca.* 420 and 520 nm (see Fig. S4-S6, Supp. Info.) which, by comparison to literature, [^{7b}] could be unambiguously attributed to the formation of *Pyr (T₁) via the TTET mechanism, which then decays on a *ca.* 10-15 μ sec timescale.

*
$$[Ru(bpy)_3]^{2+}(^{3}MLCT) + Pyr \rightarrow [Ru(bpy)_3]^{2+} + *Pyr(T_1)$$
 (3)

From the corresponding kinetic fits, a decrease in the *Pyr (T_1) lifetime upon increasing concentrations of pyrene was also found (see Table 1, entries 2-4), which we rationalised by the presence of Triplet-Triplet-Annihilation (TTA) under these conditions.

*Pyr (T₁) + *Pyr (T₁)
$$\rightarrow$$
 *Pyr (S₁) + Pyr (4)

Indeed, the occurrence of TTA was also confirmed using Time Correlated Single Photon Counting (TCSPC) fluorescence lifetimes techniques (see Fig. S8, Supp. Info.). Specifically, the ³MLCT emission of the [Ru(bpy)₃]²⁺ complex monitored at 620 nm after 450 nm excitation yielded a *ca.* 690 ns decay time, which showed excellent agreement with an observed rise in anti-stokes upconverted *Pyr (S₁) fluorescence at 390 nm. This signal subsequently decayed on the µsec timescale, providing definitive evidence for the presence of TTA.

Concurrently, the behavior of $[Ru(bpy)_3]^{2+}$ in the presence of varying initial concentrations of DIPEA was also investigated (see Fig. S9-S11, Supp. Info.). As was the case with pyrene, significant quenching of the * $[Ru(bpy)_3]^{2+}$ (³MLCT) excited state lifetime was observed, which in this case can be attributed to reductive quenching of the metal complex in the presence of the amine electron donor.

*[Ru(bpy)₃]²⁺ (³MLCT) + DIPEA
$$\rightarrow$$
 [Ru(bpy)₃]⁺ + DIPEA⁺ (5)

The photoproducts of this SET reaction are photoreduced $[Ru(bpy)_3]^+$ and DIPEA⁺. Accordingly, the appearance of the ns-TA spectrum clearly evolves over time towards that of the

 Table 1. Summary of excited state lifetime data determined by global fitting of ns-TA data under a variety of initial reaction conditions.

Entry ^[a]	[Pyrene] (mM)	[DIPEA] (mM)	*[Ru(bpy)₃]²+ (³MLCT) τ₁ (ns)	*Pyr (T₁) τ₂ (μs)	[Ru(bpy)₃]⁺ τ₃ (μs)
1	0	0	1043.3 ± 4.0	N/A	N/A
2	0.5	0	809.3 ± 5.1	13.6 ± 0.4	N/A
3	1.0	0	720.0 ± 4.2	12.3 ± 0.2	N/A
4	2.0	0	623.5 ± 4.4	11.8 ± 0.2	N/A
5	0	14	831.9 ± 5.3	N/A	38.1 ± 2.6
6	0	28	745.9 ± 7.6	N/A	32.0 ± 2.6
7	0	56	584.8 ± 5.2	N/A	26.3 ± 1.2
8	1.0	14	676.5 ± 9.2	5.8 ± 0.4	37.0 ± 4.5
9	0.5	28	636.0 ± 5.8	3.6 ± 0.3	29.0 ± 2.7
10	1.0	28	610.2 ± 7.1	3.9 ± 0.2	25.2 ± 4.9
11 ^[b]	1.0	28	576.0 ± 4.7	4.4 + 0.2	25.8 + 2 1

[a] All samples contain 0.2 mM [Ru(bpy)₃]Cl₂ as the photocatalyst in degassed DMSO. [b] Measurement conducted in the presence of 20 mM 2-bromobenzonitrile and 200 mM *N*-methylpyrrole.

 $[Ru(bpy)_3]^{\scriptscriptstyle +}$ complex, which was identified by comparison to the literature ${}^{[8]}$

The resulting ³MLCT lifetimes are also summarized (see Table 1, entries 5-7), and Stern-Volmer analysis as before (see Fig. S12, Supp. Info.) allowed K_{sv} and hence the bimolecular SET quenching rate with DIPEA as the electron donor to be evaluated as $k_{SET} = 1.31 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. A decrease in the lifetime of the $[\text{Ru}(\text{bpy})_3]^+$ complex upon increasing DIPEA concentrations is ascribed to an increase in the rate of non-geminate charge recombination due to elevated DIPEA⁺ concentrations.^[9]

 $[Ru(bpy)_3]^+ + DIPEA^+ \rightarrow [Ru(bpy)_3]^{2+} + DIPEA$

The photophysical behavior of the $[Ru(bpy)_3]^{2+}$ complex in the presence of differing concentrations of both pyrene and DIPEA was then investigated (see Fig. S3-S15, Supp. Info.). The kinetic data is summarized (see Table 1, entries 3, 6, 8-10) and an example of the observed ns-TA spectra at various time delays, together with results from global fitting analysis is shown in Fig. 1. Cursory inspection of the ns-TA data obtained in this case reveals the presence of ESA signals which can be attributed to the initially formed ³MLCT excited state, together with other evolving ESA signals from both *Pyr (T₁) and the one-electron reduced [Ru(bpy)₃]⁺ complex. By fitting the kinetic decay profile to a three exponential model, the results from global analysis allows the differing spectral features of *[Ru(bpy)₃]²⁺ (³MLCT), *Pyr (T₁) and the [Ru(bpy)₃]⁺ to be more clearly resolved in the corresponding Decay Associated Difference Spectra (DADS) shown in Fig. 1c.

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Figure 1. (a) Observed ns-TA spectra (λ_{ex} = 450 nm) at various time delays for a solution of 0.2 mM [Ru(bpy)₃]²⁺, 1.0 mM Pyrene, and 28 mM DIPEA in degassed DMSO (b) Corresponding decay kinetics at selected wavelengths and (c) global fitting analysis showing Decay Associated Difference Spectra (DADS).

This DADS data allowed the excited state lifetimes for each species with differing initial reaction conditions to be readily analyzed. For example, the initially formed ³MLCT excited state for a given *[Ru(bpy)₃]²⁺ complex can undergo either TTET or SET when both pyrene and DIPEA are present in solution, depending on the collisional reaction partner, and the DADS show these two processes occur in tandem. The quenching of the resulting *[Ru(bpy)₃]²⁺ (³MLCT) excited state lifetime is summative, as expected, and is in agreement with the previous individually evaluated K_{sv} constants, allowing the contribution of each process to also be estimated.

More importantly, the evaluated lifetime data reveals a clear decrease in lifetime of the photoreduced $[Ru(bpy)_3]^+$ complex with increasing initial concentration of pyrene (see Table 1, entries 6, 9, 10). Similarly, the *Pyr (T₁) lifetime is strongly quenched as a function of the initial DIPEA concentration (see Table 1, entries

3, 8, 10). Given the reaction of $[Ru(bpy)_3]^{2+}$ and DIPEA in isolation was shown to form the one electron reduced $[Ru(bpy)_3]^+$ complex, these two results strongly implicate an excited state reaction between these two photoproducts. Taking the available thermodynamic data and photocatalytic behavior into consideration, our ns-TA results are consistent with formation of the highly reactive pyrene radical anion (Pyr⁻) via an excited state intermolecular electron transfer reaction between these two products, which we can summarize as;

$$Pyr (T_1) + [Ru(bpy)_3]^+ → Pyr^- + [Ru(bpy)_3]^{2+}$$
(7)

Notably, this reaction is expected to be highly exergonic (*ca.* +1.23 V vs SCE) and is one of the reaction pathways proposed^[10] by König involving photochemically and/or photoredox generated reactive intermediates that may be present in the reaction mixture under catalytic conditions.

In order to revisit the possibility of a TTA mediated pathway for Pyr- radical anion generation, we have undertaken similar TCSPC lifetime measurements using the [Ru(bpy)₃]²⁺ complex in the presence of both pyrene and DIPEA. In this case we also observed evidence for TTA. However the intensity of the upconverted *Pyr (S1) fluorescence was reduced to less than 5 % of that observed in the absence of DIPEA (see Fig. S16, Supp. Info). The decrease in upconverted *Pyr (S1) fluorescence can be potentially attributed to SET quenching in the presence of DIPEA, which is thermodynamically favourable (eqn 2), and results in formation of the Pyr- radical anion via the TTA mechanism. Alternatively, the bimolecular quenching of *Pyr (T_1) with concomitantly formed [Ru(bpy)₃]⁺ (eqn 7) would decrease the *Pyr (T₁) excited state population available to undergo the TTA process, and similarly result in the observed decreased in upconverted *Pyr (S₁) fluorescence.

In order distinguish between these two possibilities, we have sought to estimate the relative contributions of TTA compared to SenI-ET quenching of the *Pyr (T1) excited state. Using a modified Stern-Volmer approach, and the concentration dependent decrease in *Pyr (T1) lifetime, we estimate the rate of bimolecular Triplet-Triplet-Annihilation as $k_{TTA} = 1.34 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (see Fig. S17, Supp. Info.). The rate constant for bimolecular SenI-ET quenching was evaluated via the concentration dependent decrease in *Pyr (T1) lifetime as a function of $[Ru(bpy)_3]^+$ ($k_{SenI-ET} = 2.2 \times 10^{11} \text{ M}^{-1} \text{ s}^{-1}$, see Fig. S18, Supp. Info.), and the latter is approximately an order of magnitude faster than k_{TTA} . Using these rate constants, we are able to estimate the proportion of the *Pyr (T1) excited state which will be guenched via the TTA compared to SenI-ET pathways (see Section 14, Supp. Info.). The results of these calculations reveal the vast majority of *Pyr (T₁) will be consumed by the SenI-ET mechanism, with only a minor proportion (ca. <5%) of *Pyr (T1) diverted towards TTA and other non-radiative processes. This is fully consistent with the >95% decrease in upconverted *Pyr (S_1) fluorescence observed experimentally by TCSPC methods. Accordingly, it appears that the TTA pathway is effectively shutdown in the presence of the one electron reduced [Ru(bpy)₃]⁺ complex, and the SenI-ET reaction is the primary source of Pyrradical anions involved in the subsequent organic photocatalysis reactions.

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Lastly, with the catalytic reaction in mind, we undertook a final ns-TA measurement (see Fig. S19, Supp. Info) using catalytically relevant concentrations of [Ru(bpy)₃]²⁺, pyrene and DIPEA in the presence of 2-bromobenzonitrile and N-methylpyrrole (see Table 1, entry 11). The resulting fit of kinetic parameters for *Pyr (T_1) and the [Ru(bpy)₃]⁺ complex are within experimental error of those in the absence of organic substrates, indicating a lack of interaction between these components. Interestingly, the *[Ru(bpy)₃]²⁺ (³MLCT) excited state lifetime is reduced by *ca.* 30 ns in the presence of 2-bromobenzonitrile and N-methylpyrrole, suggesting it may play an additional role as a potential photooxidant of the C-H arylated product. The possibility of *[Ru(bpy)₃]²⁺ (³MLCT) being involved in formation of the final product was also by suggested¹⁰ by König, although further experiments using different concentrations of organic substrate would be required to confirm this step. It is unfortunate we were not able to directly observe formation of the pyrene radical anion (Pyr-) using ns-TA spectroscopy, despite its well-known^[7c] and intense ESA signal at 495 nm. However, this may be rationalized if the rate of Pyr- formation from the two precursors as shown in eqn. 7 is slow, compared to its consumption. In this context, we note the reverse electron transfer reaction to form the pyrene ground state;

$$Pyr^{-} + [Ru(bpy)_3]^{2+} \rightarrow Pyr + [Ru(bpy)_3]^+$$
(8)

is also exergonic (*ca.* +0.77 V *vs* SCE), and we would expect this reaction to also be accelerated by Coulombic effects.^[11]

Considering all of the available spectroscopic evidence, we propose the catalytic reaction mechanism shown in Fig. 2.



Figure 2. Proposed SenI-ET mechanism showing formation of both *Pyr (T_1) and $[Ru(bpy)_3]^*$ by visible light absorption, and subsequent formation of Pyr⁻ which initiates the observed C-H arylation reaction.

In this mechanism, competing energy and electron transfer reactions using $[Ru(bpy)_3]^{2+}$ as a common light harvesting unit results in the formation of both *Pyr (T₁) and the one-electron reduced $[Ru(bpy)_3]^+$ complex, with DIPEA acting as the electron source. These excited state and one-electron reduced species are sufficiently long-lived (*ca.* 10-40 µsec) in solution, facilitating their bimolecular reaction to form the Pyr⁻ radical anion, which is able to reduce aryl halides leading to the observed C-H arylation products. Interestingly, the process we describe is indeed a two-photon process, as proposed by Ceroni,^[3] since one photon each is required to generate the *Pyr (T₁) and photoreduced [Ru(bpy)₃]⁺ complex, but operates via a very different pathway to TTA. Our

proposed mechanism also agrees with recently published results^[12] wherein an analogous photoredox reaction was proposed to mediate the Birch reduction of several different arenes. This work demonstrates that not only the primary photoredox reaction, but also the possibility of secondary reactions between components can be involved in catalytic processes, and should be considered when organic photoredox mechanisms are proposed.

Experimental Section

General. $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (bpy = 2,2'-bipyridine), pyrene, *N*,*N*-diisopropylethylamine (DIPEA), *N*-methylpyrrole, 2-bromobenzonitrile and d_6 -DMSO were obtained from Sigma Aldrich and were used as received. HPLC grade DMSO was obtained from Fisher Scientific and was dried over 3 Å molecular sieves prior to use.

Physical Methods. ¹H NMR spectra in d₆-DMSO were recorded using a Bruker Avance 500 MHz spectrometer, and were referenced to the residual solvent peak at 2.50 ppm. GC-MS was performed on a Shimadzu QP-2010 equipped with a capillary column (length: 30 m; diam.: 0.25 mm; film: 0.1 µM), using He as the carrier gas. For Transient Absorption (ns-TA) measurements, a broadband pump-probe spectrometer (EOS, Ultrafast Systems, LLC) was used, while for time-resolved emission measurements, a time-resolved fluorescence spectrometer (Halcyone, Ultrafast Systems, LLC) was utilised, operating in Time Correlated Single Photon Counting (TCSPC) mode. In both cases, an amplified laser system (Spitfire ACE, Spectra Physics) was the excitation source, delivering ca. 100 fs laser pulses at 800 nm with a 1 kHz repetition rate, which were then coupled to an OPA system (Topas Prime, Light Conversion), to deliver excitation pulses tuned to 450 nm. Samples for spectroscopic measurements were degassed by three consecutive freeze-pump-thaw cycles, had an absorbance of ca. 0.4 over the 2 mm path length used, and were stirred mechanically during each measurement. Resulting spectrophotometric data was processed using Igor Pro (Wavemetrics, Version 6.1.1.2).

Synthesis of 2-(1-methyl-1H-pyrrol-2-yl)benzonitrile. In a 5 mL, 1 cm quartz degassing cuvette equipped with a magnetic stirrer bar, 2-bromobenzonitrile (0.1 mmol, 1.0 eqv), [Ru(bpy)₃]Cl₂·6H₂O (0.001 mmol, 0.01 eqv, 1 mol %), pyrene (0.005 mmol, 0.05 eqv, 5 mol %), DIPEA (0.14 mmol, 1.4 eqv) and N-methylpyrrole (1 mmol, 10 eqv) were dissolved in 5 mL of dry d₆-DMSO. This solution was subjected to three freeze pump thaw cycles and was then backfilled with argon. The reaction mixture was irradiated at 450 nm using a monochromated Xenon arc lamp with an average power of ca. 50 mW for 18 hours. The crude reaction mixture was first analysed by ¹H NMR and GC-MS, and was then transferred to a separating funnel, where water (20 mL) and brine (5 mL) were added. The mixture was extracted with ethyl acetate (3 x 15 mL), and the combined organic layers were dried over anhydrous MgSO₄, filtered and then concentrated under vacuum. The crude product was purified using flash chromatography on silica with 3:1 (v/v) hexanes/ethyl acetate as the eluent (ca. 55% yield by NMR). ¹H NMR (500 MHz, d_6 -DMSO) δ 7.91 (ddd, J =7.8, 1.4, 0.6 Hz, 1H), 7.74 (ddd, J = 7.9, 7.5, 1.4 Hz, 1H), 7.58 (ddd, J = 7.9, 1.2, 0.6 Hz, 1H), 7.53 (td, J = 7.7, 1.2 Hz, 1H), 6.97 (ddd, J = 2.7, 1.8, 0.4 Hz, 1H), 6.31 (dd, J = 3.7, 1.8 Hz, 1H), 6.14 (dd, J = 3.6, 2.7 Hz, 1H), 3.57 (d, J = 0.3 Hz, 3H). GC-MS (EI) m/z calc'd for C₁₂H₁₀N₂: 182.08; Found: 182.90 [M+H]+.

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Keywords: SenI-ET • photoredox • catalysis • mechanism

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