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Light Excitation of a Bismuth Iodide Complex Initiates I–I Bond Formation Reactions of Relevance to Solar Energy Conversion

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Supporting Information

ABSTRACT: The titration of iodide into acetonitrile solutions of BiI_3 resulted in the formation of $[BiI_6]^{3-}$. Ligand-to-metal charge transfer (LMCT) excitation of $[BiI_6]^{3-}$ yielded a transient species assigned as the diiodide anion $I_2^{\bullet-}$ directly ligated to Bi, $[Bi(I_2^{\bullet-})I_x]^n$. With 20 ns time resolution, transient absorption measurements revealed the appearance of two species assigned on the analysis of the iodine molecular orbitals as an η^2 ligated $I_2^{\bullet-}$, $[(\eta^2\text{-}I_2)BiI_4]^{3-}$ (λ_{max} = 640 nm), and an η^1 species $[(\eta^1\text{-}I_2)BiI_4]^{3-}$ (λ_{max} = 750 nm). The rapid appearance of this intermediate was attributed to intramolecular I–I bond formation. The $[(\eta^2\text{-}I_2)BiI_4]^{3-}$ subsequently reacted with 1 equiv of iodide to yield $[(\eta^1\text{-}I_2)BiI_5]^{4-}$. Interestingly, $[(\eta^1\text{-}I_2)BiI_5]^{4-}$ decayed to ground state products with a first-order rate constant of $k = 2 \times 10^3$ s^{-1}. Under the same experimental conditions, $I_2^{\bullet-}$ in CH_3CN rapidly disproportionates with a tremendous loss of free energy, $\Delta G^\circ = -2.6$ eV. The finding that metal ligation inhibits this energy wasting reaction is of direct relevance to solar energy conversion. The photochemistry itself provides a rare example of one electron oxidized halide species coordinated to a metal ion of possible relevance to reductive elimination/oxidation addition reaction chemistry of transition metal catalysts.

Iodide photo-oxidation is of direct relevance to emerging classes of third generation photovoltaic cells,[1] particularly those based on heavy metals like lead and bismuth,[2−4] and to hydrogen gas production through HI splitting.[5,6] The chemistry and photochemistry of metal halide complexes is also of general interest[4] where a large body of literature indicates that halides form stable metal–halide bonds whereas oxidized halides do not.[7,8] Indeed, a literature review revealed only a platinum triiodide complex as a rare example of oxidized iodide ligated to a metal with relevance to oxidative-addition reactions.[9] Theoretical studies indicate other examples should exist and their identification is of broad interest.[10] Here we report a light driven method for the generation of oxidized iodide and I–I bond formation in a metal coordination sphere that yields a metal diiodide adduct $[M\text{-}(I_2^{\bullet-})]$. More specifically, ligand-to-metal charge transfer (LMCT) excitation of $[BiI_6]^{3-}$ was found to yield transiently $[Bi(I_2^{\bullet-})I_x]^{n-}$ species. Remarkably, $[(\eta^1\text{-}I_2)BiI_5]^{4-}$ was stable for half a millisecond and decayed cleanly to the ground state reactants with no evidence of the disproportionation chemistry known for solvated diiodide, $I_2^{\bullet-}$ in CH_3CN.

Shown in Figure 1 is the UV–visible absorption spectra of BiI_3 CH_3CN solution with up to 48 equiv of tetrabutylammonium iodide (data shown in Table 1). The representative absorption peak positions are listed in Table 1. The spectral data was corrected for the volume change and those spectra indicated in bold represent those assigned to BiI_3, $[BiI_4]^-$, and $[BiI_6]^{3-}$. The three species were determined by monitoring peaks and isosbestic points (Figure S1).

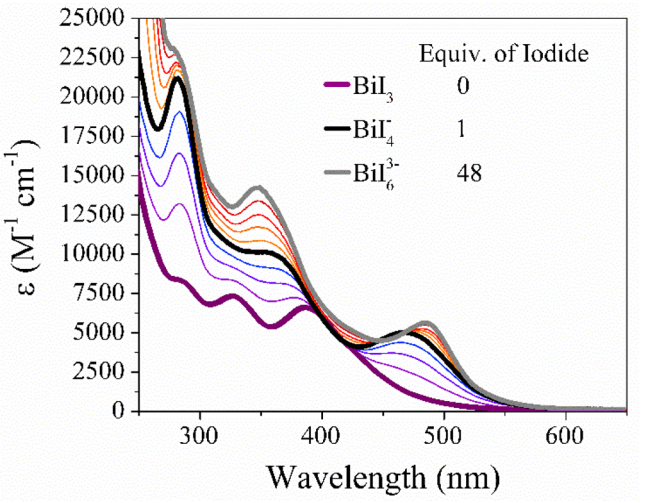

Figure 1. Absorption spectra of BiI_3 in CH_3CN titrated with tetrabutylammonium iodide (TBAI). The spectra given in bold are assigned to the indicated complexes.

Table 1. UV-vis Absorption Data of Bismuth Iodide Complexes in CH_3CN

	λ_1 (nm)	ε_1 (M^{-1} cm^{-1})	λ_2 (nm)	ε_2 (M^{-1} cm^{-1})
$[BiI]_3$	387	6600	327	7300
$[BiI_4]^{2-}$	469	5000	356	10100
$[BiI_6]^{3-}$	486	5600	350	14200

The stepwise formation constants were measured to be $K_4 > 10^6$ M^{-1} for $[BiI_4]^-$ and $K_6 = 6.4 \times 10^7$ M^{-2} for $[BiI_6]^{3-}$ in good agreement with literature values.[11,12] We note that a seven-coordinate $[BiI_7]^{4-}$ complex has previously been reported but

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was not investigated here.[11] The absorption bands are reasonably assigned as LMCT transitions that formally yield a Bi(II) and an iodine atom, $[I^{-}Bi^{III}I_n]^{x-} + h\nu \rightarrow [I{\cdot}Bi^{II}I_n]^{*x-}$. The LMCT extinction coefficients range from 5000 to 14 000 M^{-1} cm^{-1} and the $[BiI_6]^{3-}$ species absorbs light strongly through the visible region to beyond 550 nm. The specific absorption peak positions and extinction coefficients are listed in Table 1. Pulsed green light excitation, at λ = 532 nm, of $[BiI_6]^{3-}$ produced the transient absorption spectra shown in Figure 2. An advantage of

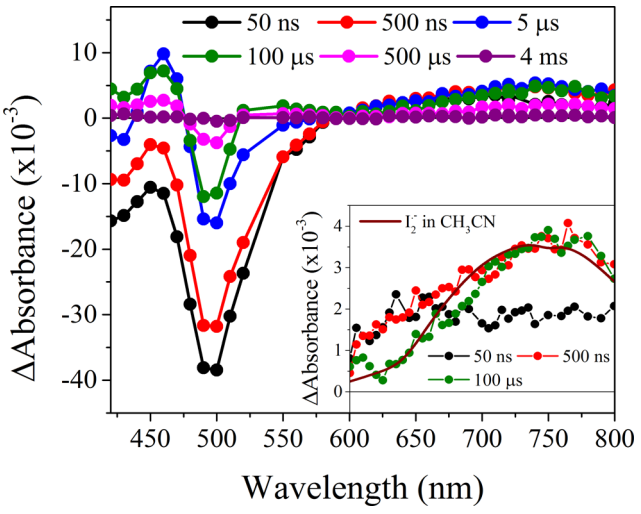

Figure 2. Transient absorption difference spectra measured at the specified time delays after pulsed 532 nm excitation (20 mJ/pulse) of BiI_3 with 6 equiv of TBAI in CH_3CN. Inset: Expansion of difference spectra between 600 and 800 nm. Overlaid in red is the spectrum of $I_2^{\bullet-}$ in CH_3CN.

these kinetic data over those of previous LMCT studies[11] was that the absorption transients cleanly returned to baseline on the millisecond time scale with no evidence of net photochemistry (Figure S2). A bleach of the LMCT bands was observed consistent with the formation of new species. A long wavelength absorption feature appeared reminiscent of that known for diiodide, $I_2^{\bullet-}$. The figure inset contrasts the low energy transient spectra with that of $I_2^{\bullet-}$ in CH_3CN. This comparison reveals a poor match, particularly in the 600−700 nm region where the transient species have significantly more amplitude.

Indeed, a careful examination of the data in the 600−800 nm region where $I_2^{\bullet-}$ absorbs light strongly revealed the presence of two transient species. The spectra observed 50 ns after laser excitation had greater amplitude in the 600−660 nm region than $I_2^{\bullet-}$ in CH_3CN did. At a 500 ns delay time, the amplitude at 630 nm remained unchanged, but the amplitude at 750 nm approximately doubled. By a delay time of 100 μs, the amplitude at 630 nm decreased and the spectra now closely resembled that of $I_2^{\bullet-}$ in CH_3CN.

The classical molecular orbital description of iodine is shown (Figure 3), which correctly predicts the $I_2^{\bullet-}$ bond order of 1/2 and the presence of three absorption bands. The SOMO-1 to SOMO gap gives rise to a $\pi^*\rightarrow\sigma^*$ absorption band in the mid-IR region that has been previously observed.[13] The absorption characterized here is assigned to the SOMO-2 to SOMO, $\pi\rightarrow\sigma^*$, that differs from the older literature that excluded this assignment based on the symmetry forbidden nature of the transition that is not relevant to the bismuth diiodide adduct.[13] A TD-DFT analysis of diiodide using multiple functionals and

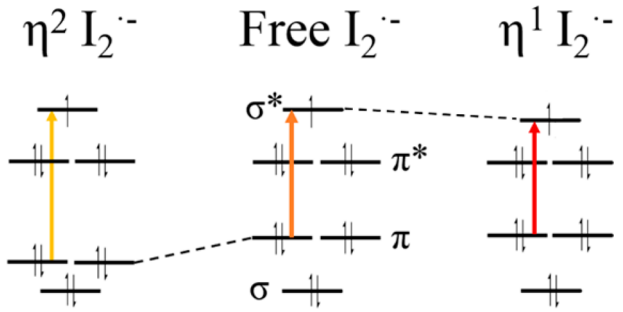

Figure 3. Simplified molecular orbital diagrams of uncomplexed $I_2^{\bullet-}$ as well as η^1 and η^2 ligated $I_2^{\bullet-}$.

basis sets (B3LYP/aug-cc-pVTZ and PBE0/6-311g** (d,p)), used previously for accurate iodine calculations,[14,15] supports the assignment of 600−800 nm band as a $\pi\rightarrow\sigma^*$ transition (Table S1). The ~640 nm absorption transient is assigned to an η^2 ligated $I_2^{\bullet-}$, $[(\eta^2\text{-}I_2)BiI_4]^{3-}$, and the 750 nm absorption to an η^1 complex, $[(\eta^1\text{-}I_2)BiI_5]^{4-}$ (Figure S3). These assignments are made based on the expectation that η^2 ligation will stabilize the iodine π orbitals through interaction with empty bismuth p orbitals whereas η^1 ligation stabilizes the σ^* through a similar interaction. Through global kinetic analysis,[16] the time dependence of the concentrations of each species was obtained, Figure 4. A description of this analysis is given in the SI.

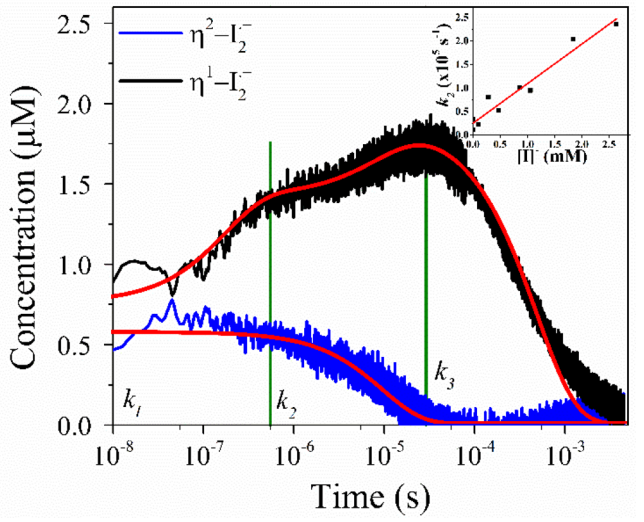

Figure 4. Modeled concentration profiles of η^1 and η^2 $I_2^{\bullet-}$ after excitation of $[BiI_6]^{3-}$ Inset: Plot of k_2 versus $[I^-]$ for the transformation from η^2 to η^1 diiodide.

The proposed mechanism for I−I bond formation shown in Scheme 1 is consistent with the spectroscopic observations described and additional kinetic studies performed as a function of the iodide concentration and the number of absorbed photons (concentration). The reactions are initiated by LMCT light absorption ($h\nu$) to yield formally Bi(II) and an iodine atom in the initially formed Franck−Condon excited state. The iodine atom is then proposed to react with iodide by intramolecular electron transfer to yield both $[(\eta^2\text{-}I_2)BiI_4]^{3-}$ (with rate constant $k_1 > 10^8\ s^{-1}$) and $[(\eta^1\text{-}I_2)BiI_4]^{3-}$, Figure 4. The transient spectral data provides clear evidence for exactly two Bi−$I_2^{\bullet-}$ adducts (Figure S3) that accurately model all the spectral data. The molecular orbital description discussed above is consistent with

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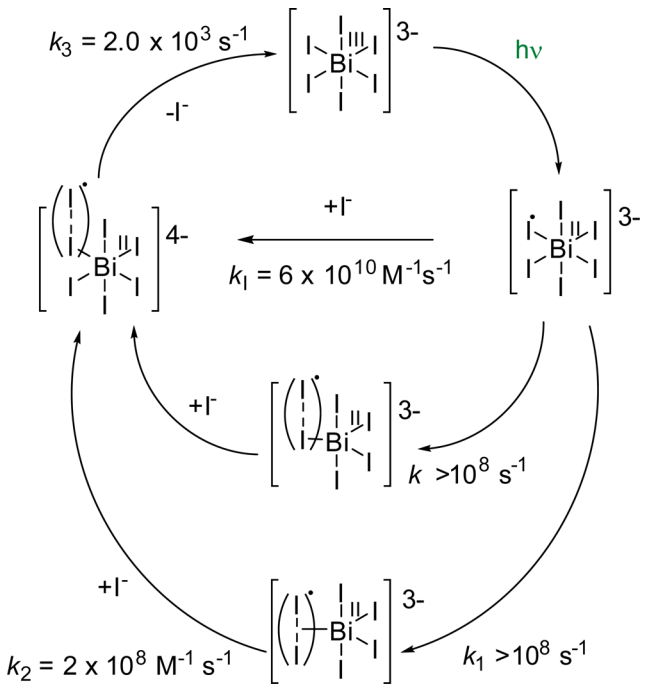
Scheme 1. Proposed Mechanism Following Iodide to Metal Charge Transfer of a $[BiI_6]^{3-}$ Species



the higher energy absorption being due to the η^2-I_2 adduct and the lower energy the η^1-I_2. The intra- versus intermolecular assignment is based on sub-20 ns appearance of these species that under these experimental conditions represents a time scale too short for diffusional intermolecular reactions. As described below, the η^2-I_2 adduct had clearly formed and saturated within the 20 ns instrument response time, whereas the formation of the η^1-I_2 adduct appeared in the first 100 ns, and then further increased as η^2-I_2 adduct reacts later, making the initial intramolecular bond formation assignment less certain particularly if some weakly associated iodide was present at the time of excitation.

The $[(\eta^2\text{-}I_2)BiI_4]^{3-}$ intermediate is proposed to react with an additional iodide to yield $[(\eta^1\text{-}I_2)BiI_5]^{4-}$. Clear experimental evidence for this reaction was illustrated by the kinetic rate constant (k_2) for loss of the η^2 species being identical to the generation of the η^1 species. Furthermore, the inset of Figure 4 shows that this reaction is first-order in iodide, $k_2 = 2 \times 10^8$ M^{-1} s^{-1}. Because the absorption features are due to intraligand $I_2^{\bullet-}$ transitions, they were not expected to be highly sensitive to the coordination number; in other words $[(\eta^1\text{-}I_2)BiI_4]^{3-}$ and $[(\eta^1\text{-}I_2)BiI_5]^{4-}$ were expected to have similar absorption spectra. Although the photochemistry is very different, we note that there is precedence for ligand coordination inducing a change in hapticity, intermolecular ligand induced η^5-η^3 ring slippage of Pt($\eta^{3/5}$-indenyl) complex.[17] Thus, with mM iodide concentrations the only transient species identified 100 μs after LMCT excitation was $[(\eta^1\text{-}I_2)BiI_5]^{4-}$.

The dissociation of iodide from $[(\eta^1\text{-}I_2)BiI_5]^{4-}$ generates the ground state reactant. Normalized kinetic data show that the rate constant k_3 was insensitive to the initial concentration of $[(\eta^1\text{-}I_2)BiI_5]^{4-}$ formed (over a factor of 2, Figure S5) and the iodide concentration (Figure S6), data that is all consistent with a unimolecular reaction. The transient data were satisfactorially described by a first-order rate constant, and revealed a remarkably slow reaction, $k_3 = 2.0 \times 10^3$ s^{-1}. Some small deviations from first-order kinetics were observed, particularly at long observation times and low iodide concentrations. These deviations, however, were small and occurred within a time-span in which the signal-to-noise ratios, at <3, became a difficult combatant in assigning any possible additional reactions. These small deviations could be due to photochemistry of low concentration species within the equilibrium of the bismuth iodide system.

Concerted two-electron transfer reactions are often invoked in reductive elimination/oxidation addition reaction chemistry of transition metal complexes.[18] However, a composite mechanism with discrete, sequential 1e$^-$ transfers can be envisioned.[19] In this regard, the $[(I_2)BiI_x]^{n-}$ species represent likely 1e$^-$ transfer intermediates in this chemistry. Reduction of the ligated diiodide by a single electron lowers the I–I bond order to zero and yields two iodide ions. Oxidation by one electron yields molecular I_2 that would be expected to dissociate. The η^2 linkage isomers would promote addition/elimination in a cis- stereochemistry about the metal and the observation of trans- products would require subsequent ligand rearrangement. Using this example as a model, mechanistic pathways for reductive elimination can be reinvestigated through the use of LMCT light excitation.

The transiently generated $[(\eta^1\text{-}I_2)BiI_5]^{4-}$ returned to ground state products with a first-order rate constant of 2.0×10^3 s^{-1}. Increasing the number of absorbed photons by up to a factor of 6 revealed no evidence for second- or higher-order reactivity, and the rate constants were insensitive to the iodide ion concentration. This is quite unlike the reactivity of $I_2^{\bullet-}$ in CH_3CN that disproportionates cleanly, $2I_2^{\bullet-} \rightarrow I_3^- + I^-$ $k = 3.3 \times 10^9$ M^{-1} s^{-1}.[20] For instance, at 10 mM concentration of diiodide, coordination of $I_2^{\bullet-}$ to bismuth enhance its lifetime by over 4 orders of magnitude. Therefore, although the transient spectrum of $[(\eta^1\text{-}I_2)BiI_5]^{4-}$ was very similar to that of $I_2^{\bullet-}$ in CH_3CN, the kinetics for relaxation to ground state products were so sufficiently different as to be distinguishing.

An intriguing question is why does the $[(\eta^1\text{-}I_2)BiI_5]^{4-}$ species live for half a millisecond? In other words, why does the Bi^{II} not rapidly reduce $I^{\bullet}$ or $I_2^{\bullet-}$? Answers to these questions remain speculative, in part because bismuth in the formal oxidation state of II has not been directly observed. Attempts to measure photoluminescence emanating from the $[BiI_6]^{3-}$ solutions have thus far been unsuccessful. In fact, LMCT excited states are generally dissociative and do not emit light. A concern was that the Bi^{II} generated by light excitation transfers the electron to another species that enables the long lifetimes of the diiodide species. However, such a process would lead to a reaction mechanism that was second-order, first-order in $I_2^{\bullet-}$ and first-order in Bi^{II}, which is contrary to experiment. Therefore, our speculation is that intersystem crossing to lower lying triplet state facilitated by the heavy bismuth metal accounts for the remarkably long-lived $[(\eta^1\text{-}I_2)BiI_5]^{4-}$ species that is indeed best formulated as an excited state.

The formation of the $[(\eta^2\text{-}I_2)BiI_4]^{3-}$ and some of the η^1 species occurred within the instrument response time of 10 ns. Such rapid I–I bond formation may occur by unimolecular electron transfer. Alternatively, LMCT light absorption could promote I–I bond formation in one concerted step. In other words, the Franck–Condon state created by light absorption may already possess the I–I bond of $I_2^{\bullet-}$, $[(I)_2\text{-}Bi^{III}I_n]^{x-} + h\nu \rightarrow [(I_2)Bi^{II}I_n]^{*x-}$. Precedence for such reactivity exists in studies of donor–acceptor iodide ion-pairs where high iodide concentrations have induced low energy absorption bands assigned to this concerted pathway.[21] In solution processing of lead

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perovskite solar cells, the solutions are the characteristic yellow color of PbI_2, yet turn black when deposited in the solid state as the methylammonium perovskites. In this structure, the iodide ions are in close-packed van der Waals contact of about 4.4 Å that can provide the electronic coupling necessary for the concerted photoexcitation.[22] At the iodide concentrations used herein, the Bi is predominantly six-coordinate and the nearest neighbor I−I distance is 4.7 Å, with the metal providing enhanced coupling. Although the data reported here does not unambiguously demonstrate such a concerted pathway, these observations warrant further study as they are highly relevant to solar energy conversion. In acetonitrile electrolytes, the $E^o(I^-/I^\bullet)$ is 300 mV more positive than is $E^o(2I^-/I_2^{\bullet-})$, resulting in concerted charge transfer transitions that occur at substantially lower energy and can harvest solar photons at longer wavelengths.

The ligated diiodide discovered herein could be utilized for applications in dye sensitized solar cells (DSSCs). Within these cells, the most commonly used redox mediator is based on a mixture of I^- and I_2.[23,24] After excited state injection, the oxidized dye is "regenerated" through iodide oxidation to yield $I_2^{\bullet-}$ that quantitatively disproportionates to yield I^- and I_3^-. This disproportionation chemistry yields iodide products that have unfavorable one-electron reduction potentials that aid in the collection of the injected electrons in the external circuit.[24] However, disproportionation comes with a tremendous 2.6 eV free energy loss for the two-electron reaction that decreases the DSSC power output and the open circuit voltage. If disproportionation could be prevented and instead $I_2^{\bullet-}$ diffused to the counter electrode where it was reduced back to iodide, this process then becomes immediately of interest as that potential difference could significantly improve device efficiency by almost a factor of 2. The results described herein indicate that metal−$I_2^{\bullet-}$ ligation represents a means by which disproportionation can be avoided.

The results of spectroscopic studies demonstrate the formation of a transiently stabilized metal diiodide adduct formed by ligand-to-metal charge transfer excitation of a bismuth iodide complex. Through spectral deconvolution a first-order rate constant of 2000 s^{-1} for diiodide decay was obtained. This relaxation pathway is unusual as diiodide is known to undergo extremely energetically favored disproportionation chemistry in fluid solution. The unexpected stabilization of $I_2^{\bullet-}$ by bismuth is tentatively assigned to spin change to a triplet state assisted by spin−orbit coupling from the heavy bismuth center. Coordination to the bismuth center stabilizes the normally unstable diiodide and its ultimate relaxation did not result in the formation of triiodide. These results provide substantial cause for further investigation into metal halide species for increasing the efficiency of the use of iodide as a redox mediator in DSSCs as well as understanding uses of iodide as a hole transport method in solid state photovoltaics.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b01793.

Titration data, UV−vis spectra used for modeling, single wavelength kinetics, TD-DFT results, and experimental details (PDF)

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Notes

The authors declare no competing financial interest.

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