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Direct $S_0 \rightarrow T_n$ Transition in the Photoreaction of Heavy-Atom-Containing Molecules

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Abstract: According to the Grotthuss–Draper law, light must be absorbed by a substrate to initiate a photoreaction. There have been several reports, however, on the promotion of photoreactions using hypervalent iodine during irradiation with light from a non-absorbing region. This contradiction gave rise to a "mystery" regarding photoreactions involving hypervalent iodine. We demonstrated that the photoactivation of hypervalent iodine with light from the apparently non-absorbing region proceeds via a direct $S_0 \rightarrow T_n$ transition, which has been considered a forbidden process. Spectroscopic, computational, and synthetic experimental results support this conclusion. Moreover, the photoactivation mode could be extended to monovalent iodine and bromine, as well as bismuth(III)-containing molecules, providing new possibilities for studying photoreactions that involve heavy-atom-containing molecules.

Introduction

Due to the increased development of light-emitting diodes (LEDs) in the 21st century, visible light is taking the place of ultraviolet (UV) light as an energy source for photoreactions in organic chemistry. The emergence of photoredox catalysis has also strongly boosted the use of visible light in this field.^[1] Hypervalent iodine has long attracted the attention of organic chemists.^[2] Photoactivation of hypervalent iodine initiates radical reactions via homolysis of the three-center, four-electron bond. Studies of photoreactions using hypervalent iodine under UV irradiation began in the 1980s.^[3] Until recently, however, the development of photoreactions using hypervalent iodine has progressed slowly.^[4,5] Maruoka et al. recently reported the difluoromethylation of heteroaromatic compounds using hypervalent iodine I (Figure 1a) under irradiation with violet light (400 nm).^[5f] Wang et al. also reported a radical cyclization with in-situ-generated hypervalent iodine II (Figure 1a) with blue LED (450 nm) irradiation.[5d] According to the Grotthuss-Draper law, light must be absorbed by a substrate or catalyst to initiate a photoreaction. The

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the document.

absorption spectra of these hypervalent iodine compounds, however, includes no apparent absorption bands in this wavelength region (Figure 1b). This contradiction gave rise to a "mystery" regarding photoreactions using hypervalent iodine. Conventionally, triplet photoreactions in organic chemistry are developed based on the $S_0 \rightarrow S_n \rightarrow S_1 \rightarrow T_1$ transition (Figure 1c). Despite reports of the spectroscopic detection of $S_0 \rightarrow T_n$ absorption transitions in the 1960s,^[6] these findings have never been widely accepted by organic chemists, probably because of the significantly unfavored property of the $S_0 \rightarrow T_n$ transition compared with the $S_1 \rightarrow T_1$ transition. Because the energy level is lower in the triplet excited state than in the singlet excited state, $S_0 \rightarrow T_n$ absorption bands are observed in a longer wavelength region than that of the $S_0 \rightarrow S_n$ transition bands, leading us to hypothesize that a direct $S_0 \rightarrow T_n$ transition, which has been considered a forbidden process, could be the key to unraveling the mystery of hypervalent iodine photoreactions.





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illustrating a general pathway for molecular excitation and our hypothesis. Ph: phenyl

Results and Discussion

To test our hypothesis, we first conducted spectroscopic experiments on the optical properties of hypervalent iodine. We chose hypervalent iodine II as a benchmark substrate, and its absorption, emission, and phosphorescence spectra were measured (Figure 2a). Emission was observed by excitation at 240 nm. The delayed emission spectrum revealed that the emission at 260-350 nm is a fluorescent component, and the peaks at wavelengths greater than 350 nm are phosphorescent components. The excitation light required for phosphorescent emission at 550 nm ranged from 230 to 410 nm, despite the fact that almost no absorption band was observed at wavelengths greater than 320 nm. In practice, phosphorescence was observed by irradiation at 360 nm (Figure S1),^[7] indicating that direct excitation to the triplet excited state occurred under these conditions. The obtained spectroscopic information suggests that weak absorption bands corresponding to the $S_0 \rightarrow T_n$ transitions should be present in this region. Thus, we measured the absorption spectra of highly concentrated solutions of II using a cell with a long optical path length to observe the $S_0 \rightarrow T_n$ absorption (Figure 2b). As a result, we could observe the absorption in the skirt of spectra extending up to 410 nm under the conditions of c (concentration) \cdot / (optical path length) = 1 mM · 100 mm. Since this absorption coincided with the excitation spectrum for phosphorescence emission at 550 nm, it was proved that the spectra at 330-410 nm having a molar extinction coefficient (ϵ) up to 30 correspond to the absorption of the direct $S_0 \rightarrow T_n$ transition. In addition, similar absorption spectra were obtained under the measurement conditions between $c \cdot I = 1$ mM \cdot 1 mm and $c \cdot I = 0.01$ mM \cdot 100 mm. Hence, the weak absorption observed using the 1 mM solution was not caused by the formation of aggregated compounds.

The absorption spectra of various hypervalent iodine compounds revealed no apparent absorption bands in the region above 360 nm (Figure 1b and 3a). On the other hand, similar spectroscopic profiles to those of II were also obtained using highly concentrated solutions of typical hypervalent iodine reagents 1, 2a, and 3d,[7] supporting the hypothesis of direct generation of the triplet excited state from the ground state using hypervalent iodine compounds. Spin-forbidden direct singlet-triplet absorption rarely occurs in organic compounds because the ε of $S_0 \rightarrow T_n$ absorption is very small; for example, the ϵ_{max} of anthracene for $S_0{\rightarrow}S_n$ absorption is ~10⁴, and the ε_{max} for S₀ \rightarrow T_n absorption is ~10⁻⁴, which means that $S_0 \to T_n$ absorption is 10^8 times weaker than $S_0 \to S_n$ absorption.^[8] In contrast, there was only a three-order-ofmagnitude difference in ε between these two transitions in the case of II; ε for the S₀ \rightarrow T_n absorption at 350 nm was 21, and ε for the $S_0 \rightarrow S_n$ absorptions at 230 and 285 nm were 13215 and 1881, respectively. The existence of internal or external heavy atoms facilitates spin-forbidden $S_1 {\rightarrow} T_1$ and $S_0 {\rightarrow} T_n$ intersystem crossing due to strong spin orbit coupling.^[8] Therefore, we reasoned that the spin-forbidden transition was relaxed due to the internal heavy-atom effect of iodine, enabling the "forbidden" transition of hypervalent iodine compounds.



Figure 2. (a) Absorption and emission properties of hypervalent iodine compound II; the vertical axis is normalized. (b) Absorption spectra of II under various conditions.



Figure 3. Absorption spectra of hypervalent iodine compounds; the wavelengths of light used for the chemical reactions in Scheme 1 are also indicated.

After the direct transition to the triplet excited state was demonstrated spectroscopically, we next performed quantum calculations to predict the $S_0 \rightarrow T_n$ absorption wavelength for hypervalent iodine using the Gaussian 16 software. After structural optimizations using density functional theory (DFT) with the MN15 functional and the basis sets SDD (for I) and cc-pVTZ (for the other atoms), time-dependent DFT (TD-DFT) calculations

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were performed using various functionals with the same basis sets.^[9] The calculated values of the longest absorption wavelengths for the $S_0 \rightarrow T_1$ transitions of various hypervalent iodine compounds are shown in Table 1. The direct $S_0 \rightarrow T_n$ absorption bands of these hypervalent iodine compounds were estimated to range between 350 and 400 nm. These were utilized as an index for setting the conditions of the corresponding photo-induced reactions.

	MN15	cam-B3LYP	mPW1PW91	ω B97XD
11	418	416	446	413
1	323	345	347	329
2a	328	352	353	335
3d	325	348	351	330
2b	346	360	377	355
2c	351	375	387	374
3a	324	348	350	331
3b	325	348	350	331
3c	331	353	357	337
3e	325	348	351	332
	326	349	353	333
3f	327	350	354	334
4	374	383	393	376

Table 1. S₀ \rightarrow T₁ absorption wavelengths for hypervalent iodine compounds predicted by TD-DFT calculations. Structural optimization: MN15/SDD (I) and cc-pVTZ (others). Basis sets for TD-DFT calculation: SDD (I) and cc-pVTZ (others).

To confirm that radical species are generated from hypervalent iodine compounds via a direct $S_0 \rightarrow T_n$ transition, radical-capture experiments were first undertaken. Compounds **1**, **2a**, and **3a–f**

were irradiated with 365-nm or 385-nm light in the presence of the 2,2,6,6-tetramethylpiperidin-I-oxyl (TEMPO) radical, affording the corresponding O-alkylated products 5a-f (Scheme 1a) in 7%-87% yields. No reaction occurred under light-shielding conditions (Scheme 1a). Dichlorination of 6 using 2b (Scheme 1b) proceeded at room temperature by irradiation with 400-nm light to obtain compound 7 in 61% yield, and a high temperature was required to promote the reaction in the dark. Spectroscopic analyses of a mixed solution of 6 and 2b revealed that no electron-donor-acceptor complex formed in this reaction,[7] indicating that solely the $S_0 \rightarrow T_n$ transition of **2b** initiated this radical process. A radical-clock experiment using 2b and 8 afforded compound 9 with a 36% yield [73% yield based on the recovered starting material (brsm) method], suggesting that homolysis of the chlorine-iodine bond occurred to give a chlorine radical via a direct $S_0 \rightarrow T_n$ transition (Scheme 1b). C–H azidation of 10 using 2c was examined by irradiation with 400-nm light at room temperature; product 11 was obtained in 40% yield (73% brsm yield), providing a rational explanation for the progress of the curious background reaction in the absence of a photocatalyst as reported by Wang et al. (Scheme 1c).^[4c] lodylbenzene 4 has a low alcohol-oxidizing ability. In fact, oxidation of 12 and 13 did not proceed in the dark. In striking contrast, the oxidation reactions proceeded smoothly under light irradiation at 400 nm, producing compounds 14 and 15 in excellent yields. The use of blue light (450 nm) or green light (510 nm) also promoted the reaction (Scheme 1d).



(nm)

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Scheme 1. Photoreactions using hypervalent iodine via a direct $S_0 \rightarrow T_n$ transition. Ts: tosyl, NPhth: phthalimide

We also synthesized a novel hypervalent iodine with an acridine skeleton 16, which was designed to absorb light of a longer wavelength than that generally absorbed by hypervalent iodine compounds.^[7] The absorption, emission, and phosphorescence spectra of 16 are shown in Figure 4a. Strong absorption bands were observed at wavelengths up to 410 nm, and weak absorption bands were observed at wavelengths up to 550 nm. Phosphorescence was observed upon irradiation at 450 nm, indicating that the weak absorption between 410 to 550 nm was $S_0 \mathop{\rightarrow} T_n$ absorption. Oxidation of 12 was examined using 16(Figure 4b). No reaction occurred under light-shielding conditions; in contrast, visible light irradiation promoted the reaction. It is worth emphasizing that although the absorbance at 400 nm was much higher than that at 450 or 510 nm, oxidation proceeded more efficiently under irradiation with 450- or 510-nm light compared with that under 400-nm light. These results indicate that the generation of a triplet excited state via a direct $S_0 \rightarrow T_n$ transition is more efficient than that via $S_0{\rightarrow}S_1{\rightarrow}T_1$ intersystem crossing.



Figure 4. (a) Absorption and emission properties of hypervalent iodine 16; the vertical axis is normalized. (b) Photo-induced oxidation of 12 using hypervalent iodine 16 via a direct $S_0 \rightarrow T_n$ transition.

If a direct $S_0 \rightarrow T_n$ transition of hypervalent iodine occurs due to the internal heavy-atom effect of iodine, it should be possible to extend this reaction mode to the visible light activation of general heavy-atom-containing molecules. As a proof-of-concept study, we examined photoreactions of monovalent iodine- or bromine-containing molecules. Spectroscopic analyses of 1-iodonaphthalene **17a** revealed that, despite the observation of an absorption band at wavelengths up to 310 nm, the excitation light for phosphorescence emission at 600 nm ranged up to 490 nm,

indicating the existence of absorption bands for direct $S_0 \rightarrow T_n$ transition between these wavelengths. In practice, we could observe weak absorption at 380–500 nm under the conditions of $c \cdot I = 1 \text{ mM} \cdot 100 \text{ nm}$, and phosphorescence was also observed by irradiation at 400 nm (Figure 5a). With these spectroscopic data in hand, radical-mediated reduction of **17a** using Bu₃SnH was examined in the absence of a radical initiator. The target reaction proceeded under irradiation with 400- or 450-nm light, providing naphthalene **18** in excellent yield. A control experiment was performed in the dark, demonstrating the positive effect of visible light irradiation on this experiment. The same phenomenon was also observed when using bromonaphthalene **17b**, and no reaction occurred in the dark (Figure 5b).



Figure 5. (a) Absorption and emission properties of 17a; the vertical axis is normalized. (b) Photo-induced reduction of 17 via a direct $S_0 \rightarrow T_n$ transition.

Furthermore, the same activation mode could be applied to organobismuth compounds. Spectroscopic analyses of triphenylbismuthine(III) 19 revealed the existence of an absorption band with an upper wavelength limit at 320 nm and that the excitation light for phosphorescence emission at 500 nm ranged up to 470 nm, indicating that light between 310 and 455 nm will trigger a direct $S_0 \rightarrow T_n$ transition (Figure 6a). The calculated prediction of the $S_0 \rightarrow T_1$ transition for **19** is 346 nm, and the energy of the T1 state of 19 was calculated to be 54.0 kcal/mol higher than that of the S₀ state. On the other hand, the bond dissociation energy of the bismuth-carbon bond in 19 was calculated to be 56.0 kcal/mol, indicating that a phenyl radical can be generated via a direct $S_0 \rightarrow T_n$ transition (Figure 6b). As shown in Figure 6c, when 19 was irradiated with 365- and 400-nm light in the presence of bis(pinacolato)diboron, 53% and 74% yields of phenyl pinacolborane 20 were synthesized, respectively,

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validating our hypothesis. In addition, without bis(pinacolato)diboron, 19 was slowly oxidized by dichloromethane to give triphenylbismuth dichloride(V) 21 in 42% yield. These results strongly suggest that the participation of a direct $S_0 \rightarrow T_n$ transition in photoreactions will be broadly applicable to heavy-atom-containing molecules.



Figure 6. (a) Absorption and emission properties of triphenylbismuthine(III) 19; the vertical axis is normalized. (b) Energy diagram of triplet state and bond dissociation of 19. Calculations were performed with mPW1PW91/SDD (for Bi) and cc-pVTZ (for the other atoms). (c) Radical reactions of 19 via a direct $S_0 \rightarrow T_n$ transition. (BPin)₂: Bis(pinacolato)diboron

Conclusion

In summary, we have demonstrated that photoactivation of hypervalent iodine with light of an apparently non-absorbing

wavelength region proceeded via a direct $S_0 \rightarrow T_n$ transition, which been, until now, considered a forbidden process. has Spectroscopic and experimental measurements support our conclusion. Moreover, proof-of-concept studies involving photoinduced radical reactions of halonaphthalenes and triphenylbismuthine revealed that this reaction mode could extend to monovalent iodine and bromine, as well as bismuth(III)containing molecules. These findings present new possibilities for the study of photoreactions involving heavy-atom-containing molecules. Further studies on the generality and applicability of this photoactivation mode are in progress.

Supporting Information. Experimental procedures and spectral data (PDF). This material is available free of charge via the Internet.

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Keywords: hypervalent iodine • heavy-atom-containing molecule • photoreaction • $S_0 \rightarrow T_n$ transitions

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