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Article

Chloride Oxidation by One- or Two-Photon Excitation of *N*-Phenylphenothiazine

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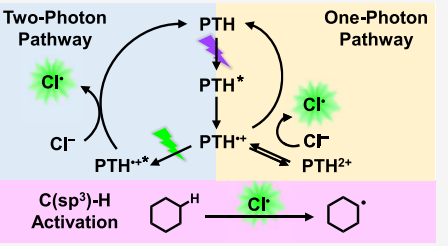
ABSTRACT: Chloride oxidation has tremendous utility in the burgeoning field of chlorine-mediated C−H activation, yet it remains a challenging process to initiate with light because of the exceedingly positive one-electron reduction potential, $E°$ ($Cl^{\bullet/-}$), beyond most common transition-metal photooxidants. Herein, two photocatalytic chloride oxidation pathways that involve either one- or consecutive two-photon excitation of *N*-phenylphenothiazine (PTH) are presented. The one-photon pathway generates $PTH^{\bullet+}$ by oxidative quenching that subsequently disproportionates to yield PTH^{2+} that oxidizes chloride; this pathway is also accessed by the electrochemical oxidation of PTH. The two-photon pathway, which proceeded through the radical cation excited state, $^2PTH^{\bullet+}$*, was of particular interest as this super-photooxidant was capable of directly oxidizing chloride to chlorine atoms. Laser flash photolysis revealed that the photooxidation by the doublet excited state proceeded on a subnanosecond timescale through a static quenching mechanism with an ion-pairing equilibrium constant of 0.36 M^{-1}. The PTH photoredox chemistry was quantified spectroscopically on nanosecond and longer time scales, and chloride oxidation chemistry was revealed by reactivity studies with model organic substrates. One- and two-photon excitation of PTH enabled chlorination of unactivated C(sp^3)−H bonds of organic compounds such as cyclohexane with substantial yield enhancement observed from inclusion of the second excitation wavelength. This study provides new mechanistic insights into chloride oxidation catalyzed by an inexpensive and commercially available organic photooxidant.



INTRODUCTION

Chlorine atoms have long been known as a powerful tool for C−H activation yet historically have seen little use in practical applications due to the harsh reaction conditions necessary to generate $Cl^{\bullet}$. Over the last decade, a number of groundbreaking studies have demonstrated facile chloride oxidation using photoredox catalysts, which have enabled new approaches to functionalize inert C−H bonds.[1−12] Additionally, environmentally motivated applications rely on chloride oxidation as an important fundamental process for HCl splitting to store solar energy[13−15] or for electric gradient generation for sea water desalination.[16−19] However, the vast majority of these examples rely on noble metal photocatalysts to generate chlorine atoms because the one-electron reduction potential, ($Cl^{\bullet/-}$), requires an incredibly potent photooxidant.[20−22] Indeed, chloride ions are so redox inert that they are frequently used as counterions for common photocatalysts such as ruthenium polypyridyl compounds.[23,24] Synthesizing ruthenium or iridium coordination compounds that are strong photooxidants requires skillful ligand engineering[1,25−28] and such catalysts often suffer from stability issues.[29−31] Moreover, photocatalysts based on noble metals are impractical at scale given the low natural abundance of these rare elements. Herein, we report a rare example of light-induced chloride oxidation catalyzed by an inexpensive, commercially available organic photocatalyst through unconventional one- and two-photon pathways.

In recent years, molecular doublet excited states of organic photocatalysts, which can be generated from consecutive light excitation, have been used to great avail as potent photoreductants in photoredox catalysis;[32−37] however, their use as photooxidants remains relatively rare.[38−41] Phenothiazine and its derivatives are one of the few radical cations studied for their oxidizing excited state properties.[42,43] In this study, we show that two-photon excitation of *N*-phenylphenothiazine (PTH) generates the highly oxidizing doublet excited state, $^2PTH^{\bullet+}$*, which catalyzes the energy-demanding oxidation of chloride to the chlorine atom (Scheme 1). Two-color two-pulse laser flash photolysis demonstrated the rapid subnanosecond electron transfer process. Our results also suggest a second, albeit less efficient, mechanism of chloride oxidation occurs in competition with the two-photon pathway. Activation of C(sp^3)−H bonds in a series of substrates was achieved by steady-state illumination of PTH, demonstrating the potential utility of this approach to synthetic chemistry applications.

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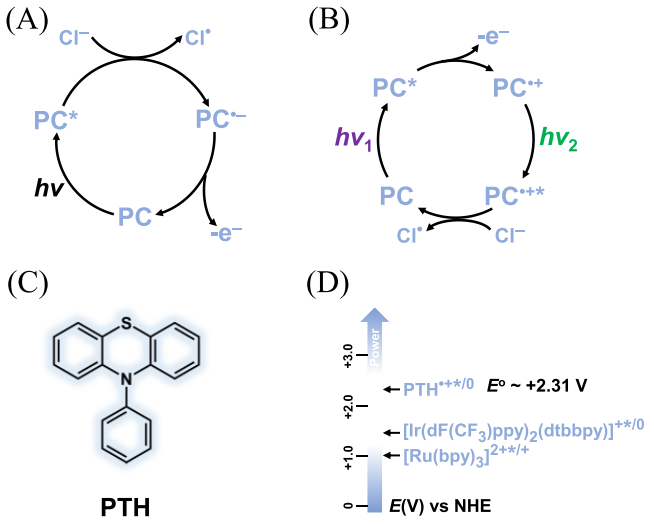
Scheme 1. Conventional Photoredox (A) and Two-Photon (B) Mechanisms for Halide Oxidation and Excited-State Reduction Potentials for Prototypical Photocatalysts (C,D)



RESULTS

The absorbance spectrum of PTH in CH_3CN displayed UV bands characteristic of $\pi \rightarrow \pi^*$ transitions at 255 and 320 nm (Figure 1). Strong room temperature fluorescence centered around 450 nm decayed with a lifetime of 3.0 ns, Figure S1, which was in good agreement with previously published data.[44] Cyclic voltammetry experiments showed a reversible PTH oxidation of $E°(PTH^{\bullet+/0})$ = 0.92 V vs NHE and a second irreversible oxidation for ($PTH^{2+/\bullet+}$) at 1.59 V vs NHE (estimated from the half anodic peak height) in CH_3CN electrolyte solutions (Figure S2). Spectroelectrochemistry measurements revealed that as the potential bias was increased from 0 to 1.13 V vs NHE, new absorption features assigned to $PTH^{\bullet+}$ were observed at 514, 772, and 864 nm, with concomitant loss of the ground-state absorbance. The spectroelectrochemical data were fully consistent with the absorbance of $PTH^{\bullet+}$ obtained from chemical oxidation by $Cu(ClO_4)_2$. The energy stored in the excited state ($E_{0,0}$) for $PTH^{\bullet+}$* was extracted from the intersection of the absorption spectrum and previously reported photoluminescence,[43] $E_{0,0}$ = 1.39 eV. The excited state redox potential for the doublet excited state $PTH^{\bullet+}$* was then approximated using the equation $E°(PTH^{\bullet+*/0}) = E°(PTH^{\bullet+/0}) + E_{0,0}$ = 2.31 V vs NHE.

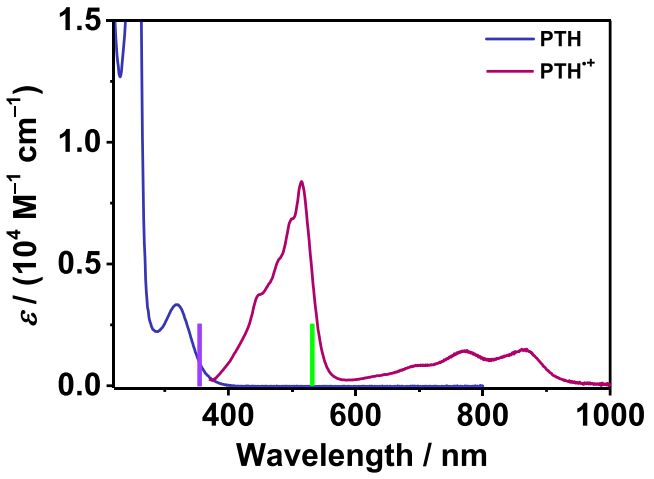


Figure 1. Molar extinction coefficients of PTH and the oxidized $PTH^{\bullet+}$ in CH_3CN. Purple and green bars show the excitation wavelengths utilized to access the two-photon chloride oxidation pathway.

Transient absorption (TA) spectra were collected following pulsed-laser excitation (λ_{ex} = 355 nm) of PTH dissolved in argon-purged and aerated CH_3CN (Figure 2A and B, respectively). The argon-saturated spectra displayed a strong feature at 460 nm assigned to absorbance of ^{3}PTH* based on the previously reported triplet excited state of the parent phenothiazine (PTZ) complex.[45] In aerated CH_3CN, the TA spectra recorded at short time delays showed a similar absorbance at 460 nm with an additional absorbance feature centered at 510 nm. By 500 ns, the feature at 460 nm fully decayed and only the absorbance at 510 nm remained; spectra at time delays ≥500 ns were fully normalizable—indicative of only one state—and were fully consistent with the $PTH^{\bullet+}$ absorption spectrum obtained from spectroelectrochemistry. Formation of $PTH^{\bullet+}$ was only observed in aerated PTH solutions, indicating that dioxygen served as an electron acceptor. It should be noted that at long time delays in the argon-saturated spectrum, a small shoulder at 510 nm became more evident, attributed to PTH ionization forming $PTH^{\bullet+}$ and a solvated electron, as was previously reported for PTZ.[42] Because the presence of ^{3}PTH* introduced additional spectral complexities that were not of primary interest to the present study, all subsequent kinetic studies unless otherwise specified were performed under oxygen-saturated environments, where ^{3}PTH* was nearly quenched on the nanosecond time scale.

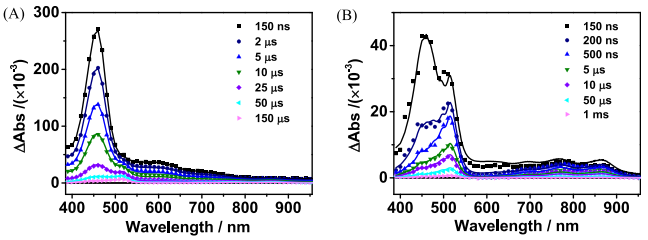


Figure 2. Absorption difference spectra of PTH in argon-purged CH_3CN (A) or aerated CH_3CN (B) after pulsed laser excitation (λ_{ex} = 355 nm) at the indicated delay times. Overlaid solid curves on the transient spectra at each delay time are the simulations based on linear combinations of the ^{3}PTH* spectrum obtained from (A) and the $PTH^{\bullet+}$ spectrum obtained from spectroelectrochemistry.

The TA spectra recorded in the presence of chloride showed the same absorbance features as were observed in the absence of chloride (Figure S3). However, single wavelength kinetics monitored at 510 nm indicated that $PTH^{\bullet+}$ absorbance decayed more slowly in the presence of the first aliquot of TBACl. A similar behavior was observed with the addition of $TBAClO_4$, albeit to a lesser extent, suggesting that an increased ionic strength retards recombination, although the precise origin of this behavior is not fully understood. Interestingly, additional aliquots of chloride led to a decrease in $PTH^{\bullet+}$ lifetime with a first-order concentration dependence in the chloride concentration, indicating a new $PTH^{\bullet+}$ redox reaction in the presence of chloride.

^{1}H NMR was used to probe whether net chemistry occurred between TBACl with $PTH^{\bullet+}$. Chemical oxidation of PTH was

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performed by stoichiometric addition of $Cu(ClO_4)_2$, which resulted in the disappearance of all the aromatic hydrogen resonances. Subsequent addition of excess TBACl to the NMR sample led to complete regeneration of the hydrogen signals corresponding to PTH (Figure S4). While this would ostensibly indicate reduction of $PTH^{\bullet+}$ by chloride, the one-electron potential for $E°(Cl^{\bullet/-})$ in CH_3CN has been crudely estimated as 1.46 V vs NHE;[20,27] therefore, reduction of $PTH^{\bullet+}$ by chloride is strongly thermodynamically disfavored.

Cyclic voltammetry experiments where tetrabutylammonium chloride (TBACl) was titrated into a solution of PTH led to a progressively less reversible $PTH^{\bullet+/0}$ redox couple, indicated by complete loss of the cathodic reduction return feature in the presence of 60 mM TBACl (~3 equiv) (Figure 3).

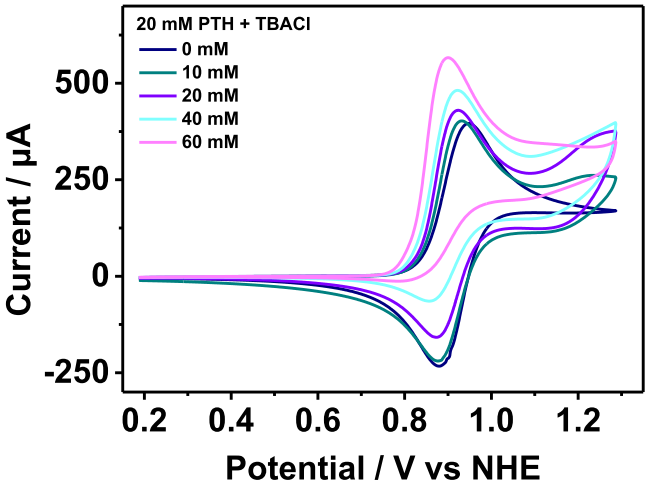

Figure 3. Cyclic voltammograms of PTH in 0.1 M $TBAClO_4$ CH_3CN with the indicated TBACl concentrations.

Interestingly, increasing the chloride concentration led to an increase in the anodic current, consistent with a catalytic reaction mechanism in which chloride regenerates PTH^0. Given the reduction potentials of the species involved, an endergonic reaction between $PTH^{\bullet+}$ and Cl^- seems highly unlikely. Indeed, similar voltammetry experiments in which PTH was replaced by $[Ir(ppy)_3]$, where ppy is phenylpyridine, showed no evidence for chloride oxidation, even though it has a more positive reduction potential, $E°(Ir^{IV/III})$ = 0.95 V vs NHE (Figure S2D). Taken together, the most compelling explanation is a previously postulated disproportionation reaction,[46] $2PTH^{\bullet+} \rightleftharpoons PTH + PTH^{2+}$, where PTH^{2+} is capable of thermally oxidizing chloride in CH_3CN. Because the first reversible oxidation of $PTH^{\bullet+/0}$ precedes the second irreversible $PTH^{2+/\bullet+}$ oxidation, the disproportionation equilibrium strongly favors $PTH^{\bullet+}$. However, chloride oxidation shifts the equilibrium toward the direction of disproportionation. A kinetic model for the disproportionation reactivity observed in the presence of chloride was derived and shown in the Supporting Information. Fitting the TA kinetics to this model provided a disproportionation equilibrium constant of 5.5×10^{-8} M^{-1} (Figure S5).

A two-photon, two-color excitation pulse sequence was used to generate $^2PTH^{\bullet+}$*, as indicated in the Figure 4A inset. The first laser pulse at 355 nm generated the long-lived $PTH^{\bullet+}$ from PTH* as described above. The second pulse at 532 nm was delayed by 500 ns relative to the first pulse to generate $^2PTH^{\bullet+}$* from the transiently generated $PTH^{\bullet+}$. Figure 4A

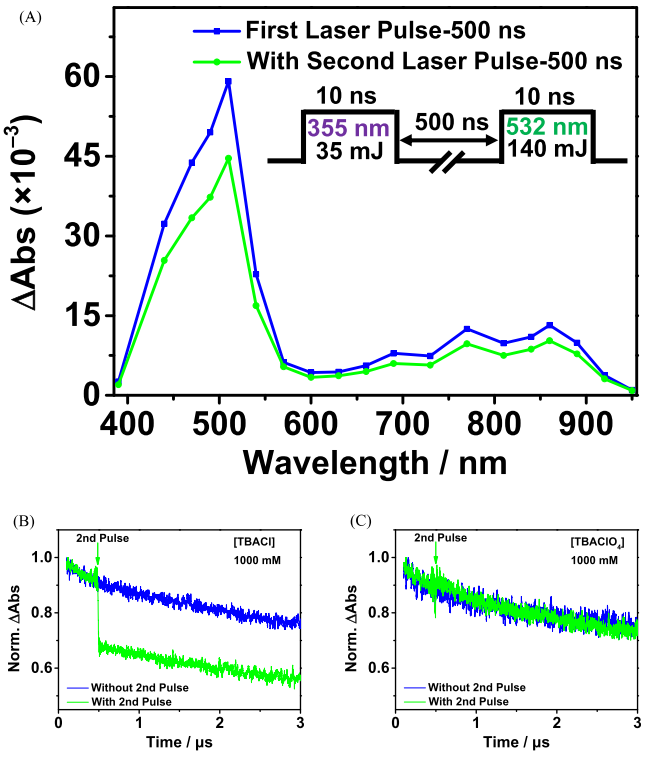

Figure 4. (A) Absorption difference spectra of PTH in the presence of 1000 mM TBACl in a two-pulse experiment with a pre-second pulse spectrum shown in blue and a post-second pulse spectrum shown in green (inset: the two-pulse sequence). Transient kinetic data for the oxidized PTH monitored at the probe wavelength of 510 nm in a two-pulse experiment with (B) 1000 mM TBACl or (C) 1000 mM $TBAClO_4$ in the CH_3CN solution. Traces in blue are without the second laser pulse excitation and the traces in green are with the second laser pulse delayed by 500 ns after the first laser pulse.

shows the TA spectra of PTH in the presence of 1000 mM TBACl immediately before and after the second laser pulse, where the transient absorbance at a given wavelength are denoted as ΔAbs_{PP} (pump-probe) and ΔAbs_{PPP} (pump-pump-probe), respectively. The second laser pulse did not generate any new absorbance features, but a substantial bleach of the $PTH^{\bullet+}$ absorption was observed (Figure 4B). Kinetics monitored at 510 nm showed that titration of TBACl ranging from concentrations of 100 to 1000 mM resulted in progressively larger bleaches directly following the second pulse (Figure S6). A control experiment where TBACl additions were replaced by the redox inert $TBAClO_4$ exhibited negligible change in absorbance upon the second laser pulse (Figure 4C). The ratio of $\Delta Abs_{PP}/\Delta Abs_{PPP}$ versus TBACl yielded a linear Stern−Volmer type plot, indicating a reaction that was first order in chloride concentration with a slope of K_S = 0.36 M^{-1} (Figure 5).

Steady-state photolysis of PTH and TBACl was performed in the presence of a halogen atom trap, 1,1-diphenylethene (DPE).[47,48] Continuous irradiation with 390 and 532 nm light through two sides of the sample yielded the photoproduct where one chlorine atom was added to DPE, identified by gas chromatography−mass spectrometry (GC−MS) (Figure S7). Control experiments indicated that irradiation with exclusively 390 nm light generated some chlorine-substituted DPE but with a significantly diminished yield, which is consistent with trace chlorine-atom formation from the aforementioned

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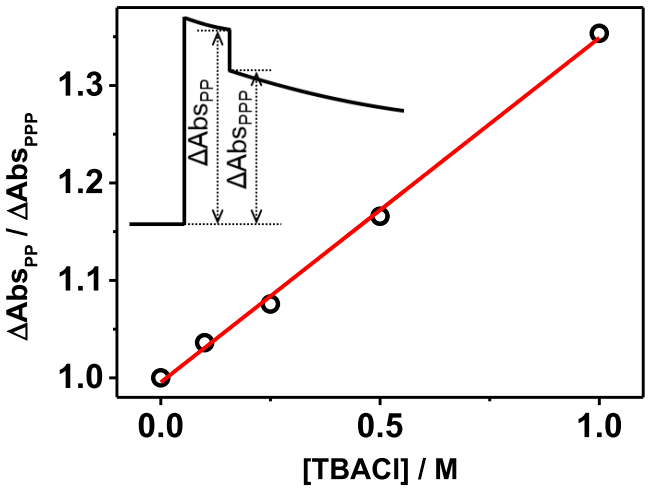

Figure 5. Stern−Volmer plot based on the two-pulse experiment upon titration of TBACl. The subscripts PP stands for pump-probe and PPP stands for pump-pump-probe. Inset: schematic illustration of the two quantities ΔAbs_{pp} and ΔAbs_{ppp}. See text for further details.

disproportionation mechanism. Addition of TBACl and DPE to electrochemically generated $PTH^{\bullet+}$ under stoichiometric conditions also led to the formation of chlorine-substituted DPE, providing further evidence for disproportionation reactivity even in the absence of light. Additional controls demonstrated that all three chemical components—PTH, DPE, and TBACl—were necessary to detect the chlorinated photoproduct. While the multiple chloride oxidation mechanisms are of fundamental interest, it is important to note that the yield of chlorine-substituted DPE was 85% higher under two-color illumination.

Successful chlorine-atom trapping experiments inspired us to determine whether one- and two-photon excitation of PTH could enable reactivity with unactivated $C(sp^3)$−H bonds using cyclohexane as a model substrate. Photolysis results from other substrates including toluene, 1,4-dioxane, and cycloheptane that represent good structural diversity are also shown in the Supporting Information (Figure S8). Initial trials conducted under identical conditions as the previously described steady-state photolysis experiments yielded C−H activation products where oxygenation of the cyclohexane was observed due to the reaction of the transient carbon radical (Figure 6) with dioxygen, as has been previously observed.[5] Replacing dioxygen with CCl_4 as the sacrificial electron acceptor enabled generation of the chlorinated C−H activation photoproduct, chlorocyclohexane.[49] (Note that 405 nm light was used in place of 390 nm to avoid direct excitation of CCl_4.) Consistent with our other steady-state photolysis experiments, inclusion of the second light source at 532 nm that exclusively excited $PTH^{\bullet+}$ resulted in 38% increase of the chlorination product (Figure 6). The proposed mechanism for halogenation of cyclohexane starts with hydrogen atom abstraction by the photogenerated chlorine atom in which HCl and cyclohexane radicals were the secondary photoproducts. The final chlorocyclohexane product was obtained by cyclohexane radical either abstracting a chlorine atom from CCl_4 or capturing another photogenerated chlorine atom in the solution. It should be noted that the actual chlorine atom source could also be from $Cl_2^{\bullet-}$ or Cl_3^- due to multiple equilibria among chlorine species in the precense of excess chloride.[22]

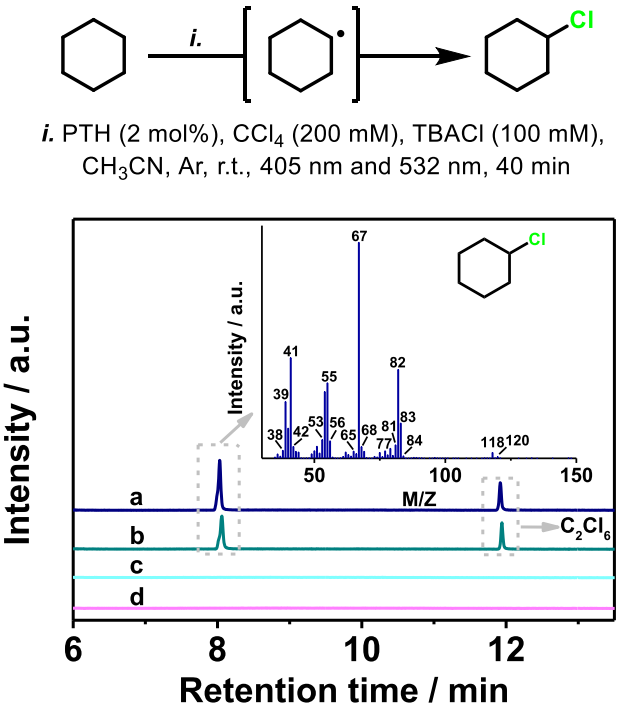

Figure 6. GC−MS analysis of the photocatalytic chlorination reaction of an unactivated $C(sp^3)$−H bond on cyclohexane. (a) PTH + CCl_4 + TBACl + cyclohexane + 405 and 532 nm irradiation, (b) PTH + CCl_4 + TBACl + cyclohexane + 405 nm irradiation, (c) PTH + TBACl + cyclohexane + 405 nm irradiation, and (d) CCl_4 + TBACl + cyclohexane + 405 nm irradiation. (PTH: 20 mM, CCl_4: 200 mM, TBACl: 100 mM, Cyclohexane: 1 M in CH_3CN, Ar, r.t., 405 nm: 100 mW, 532 nm: 1.3 W, 40 min). Inset shows the mass spectrum for the photoproduct detected at the retention time of 8.06 min.

DISCUSSION

The electrochemical, spectroscopic, and reactivity studies reported herein provide compelling evidence for a two-photon technique to generate chlorine atoms in oxygenated solutions. The first photon, $h\nu_1$, creates the oxidized donor $PTH^{\bullet+}$ and the second photon, $h\nu_2$, selectively excites $PTH^{\bullet+}$ to generate a super-photooxidant $^2PTH^{\bullet+}$* that oxidizes chloride on a sub-10 ns time scale. The complete proposed mechanism is shown in Scheme 2. Interestingly, there was clear evidence for some chloride oxidation in the absence of the second photon and when $PTH^{\bullet+}$ was generated electrochemically. Below, we discuss this $PTH^{\bullet+}$ reactivity followed by a more detailed analysis of the two-photon mechanism.

The lifetime of the photogenerated $PTH^{\bullet+}$ decreased when the chloride concentration was increased from 100 to 1000 mM. Direct chloride oxidation by $PTH^{\bullet+}$ is thermodynamically uphill by >500 mV and hence an unlikely pathway. Early studies on phenothiazine radical cations suggested that chloride may substitute the aromatic hydrogen atoms through nucleophilic attack;[50] however, ^1H NMR analysis reported here revealed no evidence for net photochemistry. Instead, a more likely disproportionation mechanism is proposed that generates the two-electron oxidized donor, $2PTH^{\bullet+} \rightleftharpoons PTH + PTH^{2+}$.[46] The PTH^{2+} is a potent oxidant competent of generating chlorine atoms that reacted with the olefin trap 1,1-diphenylethene. Hence, light-initiated or electrochemical generation of $PTH^{\bullet+}$ resulted in chloride oxidation, although the two-photon approach described below results in a markedly higher yield.

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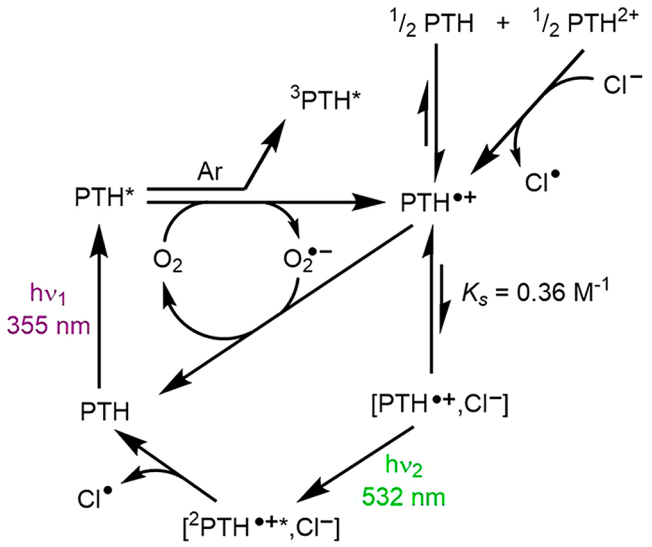
Scheme 2. Proposed Mechanism of Chloride Oxidation by Multiple PTH-Mediated Pathways



Green light excitation of $PTH^{\bullet+}$ formed the extremely potent photooxidant $^2PTH^{\bullet+}$* with an excited state reduction potential >2.3 V vs NHE. The excited state lifetime of $^2PTH^{\bullet+}$* was previously reported to be 36 ps,[43] which precludes dynamic (diffusional) quenching at the concentrations utilized. Fortunately, this cation forms a weak ion pair with chloride, K_S = 0.36 M^{-1}, in CH_3CN that rapidly reacts without diffusional limitations, $k_{et} > 10^8$ s^{-1}, to regenerate the PTH ground state. While the spectroscopic data provided compelling evidence of reductive electron transfer and $^2PTH^{\bullet+}$* → PTH conversion, the chloride oxidation products were not observed spectroscopically. Previous pulse radiolysis studies have indicated that aqueous chloride oxidation yields the chlorine atom (Cl) and the dichloride radical anion ($Cl_2^{\bullet-}$).[51,52] Both products are expected due to the $Cl^- + Cl \rightleftharpoons Cl_2^{\bullet-}$ equilibrium. For simplicity, only the chlorine atom is shown in Scheme 2, but a similar equilibrium is expected in CH_3CN. In any event, both of these oxidized species absorb weakly in the ultraviolet region and were not detected following two-photon excitation.

Direct evidence for the presence of oxidized chloride species was provided by reactivity studies first with a halogen atom trap, 1,1-diphenylethene (DPE), and then with substrates containing unactivated C(sp^3)−H bonds. Chlorine-substituted DPE was observable from the reaction of TBACl with electrochemically generated $PTH^{\bullet+}$ by the aforementioned disproportionation pathway. Illumination of PTH with only blue light generated some chlorinated photoproduct, which was also attributed to reactivity enabled by disproportionation. An additional possibility is that while the blue light absorbance of $PTH^{\bullet+}$ is small, prior research has reported excitation at 390 nm to form $PTH^{\bullet+}$*, although undoubtably with lower efficiency than 532 nm.[38] Addition of the green light source to photolysis experiments ensured generation of $^2PTH^{\bullet+}$*, which enabled the two-photon pathway in Scheme 2. Two-photon illumination resulted in chlorinated photoproduct yields that were enhanced by 85 and 38% for DPE and cyclohexane, respectively, relative to single-wavelength illumination. The generality of this approach was established using the additional substrates toluene, 1,4-dioxane, and cycloheptane, which resulted in analogous C−H activation and chlorination in two-photon photolysis experiments. Reactivity studies demonstrating chlorination of vinylic, benzylic, α-alkoxy, and unactivated aliphatic C−H bonds, coupled with time-resolved absorption studies, provided compelling evidence that $^2PTH^{\bullet+}$* was reductively quenched by chloride to form the chlorine atom intermediate as the primary photoproduct.

CONCLUSIONS

In conclusion, the organic photocatalyst PTH was shown to photo-oxidize chloride in CH_3CN solutions. Two photocatalytic pathways that generate potent oxidants, PTH^{2+} or $^2PTH^{\bullet+}$*, were identified. The former was generated by one-photon excitation of PTH followed by disproportionation, whereas the latter $^2PTH^{+}$* was formed by a consecutive two-photon excitation pathway. Mechanistic studies based on two-pulse two-color laser flash photolysis experiments revealed that chloride photo-oxidation occurred on a subnanosecond time scale through an ion pair at high chloride concentrations. While transient kinetic studies were based on a timed sequence of two laser pulses, this photoredox chemistry was also shown to be operative with two steady-state light sources through the activation of C(sp^3)−H bonds for accelerated synthesis of a variety of chlorinated organic compounds. The two-photon approach to chloride oxidation is a more desirable option for synthetic and environmental applications because of the panchromatic light absorption by the oxidized PTH to yield $^2PTH^{+}$* as a super-photooxidant. The study demonstrates that the generation of a potent organic radical cation excited state enables rapid chloride oxidation to the highly reactive and synthetically useful chlorine atom intermediate.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c07107.

Experimental details; additional spectroscopic and electrochemical characterizations; kinetic model derivation; and GC−MS product analysis for photolysis (PDF)

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Notes

The authors declare no competing financial interest.

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