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Disulfide-Catalyzed Visible-Light-Mediated Oxidative Cleavage of C=C Bonds and Evidence of an Olefin-Disulfide Charge-Transfer Complex

Yuchao Deng,^[a,b,c] Xiao-Jing Wei,^[d] Hui Wang,^[a] Yuhan Sun,^[a,b] Timothy Noël,^[d] and Xiao Wang^{*[a,e]}

Abstract: A photocatalytic method for the aerobic oxidative cleavage of C=C bonds has been developed. Electron-rich aromatic disulfides were employed as photocatalyst. Upon visible-light irradiation, typical mono- and multi-substituted aromatic olefins could be converted to ketones and aldehydes at ambient temperature. Experimental and computational studies suggest that a disulfide-olefin charge-transfer complex is possibly responsible for the unconventional dissociation of S–S bond under visible-light.

The oxidative cleavage of olefins (OCO) is a widely applied transformation in organic synthesis, since it introduces oxygen-containing functional groups such as ketones and aldehydes from inexpensive olefinic feedstock.^[1] Despite the simplicity of the reaction, a practical and mild OCO method is still one of the long-sought goals in the development of modern chemical methodologies. One of the most popular methods for this transformation is still the old-fashioned ozonolysis,^[2] which requires an ozone generator and displays serious safety issues due to the toxicity of O₃. Modern OCO reactions include methods employing stoichiometric metal or non-metal reagents that are either toxic or strongly oxidizing,^[1] or methods that utilizing molecular oxygen as a safer and cleaner oxidant in combination of catalytic amount of transition-metal complexes^[3–5] or heat-initiated radical precursors (NHPI,^[6] AIBN,^[7] etc.). Recently, photochemical OCO methods have been reported with the photon as a traceless reagent and a green source of energy.^[8–12] In general, these methods required UV-light, or catalysts that are toxic^[8] or metal-based,^[9] or a demanding oxidative photoredox catalyst to be SET-reduced by the olefin.^[10–12] Alternatively, it would be attractive to seek a non-metal photocatalyst that functions via a non-redox/sensitization

mechanism, and preferably with a reduced cost than most photocatalysts. Herein, we report a visible-light aerobic OCO method that utilizes inexpensive aromatic disulfide as photocatalyst (Scheme 1).

Scheme 1. Summary of previous OCO methods

Several previously reported radical-catalyzed OCO reactions involved the formation of a dioxetane that decomposes to give the product aldehyde or ketone.^[3,6,7] In seeking a photo-initiated radical that could reversibly add to the C=C bond, we envisioned that the thiyl radical generated by the photolysis of disulfide could serve as an ideal catalyst.^[13,14] Recently, examples of disulfide-catalyzed photoreactions were reported, in which disulfide undergoes photolysis to catalyze the diboration of terminal alkynes,^[15a] or the reduction of a carbon–halide bond with NHC-borane,^[15b] or the [3+2] cycloaddition.^[15c] They required light from the UV-region because the dissociation of typical aromatic S–S bond cannot occur under visible-light.^[16]

In the hope of establishing a photocatalytic OCO method with visible-light instead of the harmful and equipment-demanding UV light, we were intrigued by the acceleration effect in the thiol-olefin co-oxidation (TOCO) reported and studied in-depth decades ago.^[17–21] In the presence of an olefin, the overall rate for the oxidation-addition sequence is significantly faster than the SET oxidation of thiol alone, due to the formation of an olefin-thiol charge-transfer complex (CTC) (Scheme 2).^[17,18] To the best of our knowledge, the same effect between olefin and disulfide has not been reported to date. Recently, photochemical activity of *in situ* formed electron donor-acceptor complex (EDA complex)^[22–24] has been reported by Melchiorre,^[25] in which two photo-inactive species transiently associate together to form a complex that is photo-active. Therefore, we envisioned that an analogous effect of TOCO/CTC might exist between disulfide and olefin, which could lead to a more feasible S–S bond photolysis by visible-light in the presence of an olefin (Scheme 2).

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Difficulty of photolysis for most diaryl disulfides under visible-light

Thiol-olefin co-oxidation (TOCO) via a charge-transfer complex

Proposed analogous effect between olefin and disulfide

Scheme 2. Thiol-olefin co-oxidation (TOCO) and possible analogous effect between olefin and disulfide

We initiated our study with a simple experiment, in which the MeCN solution of α -methylstyrene (**1a**) and bis(4-methoxyphenyl) disulfide (**S1**, 5 mol%) was placed under light generated from a white LED lamp and stirred for 16 h with the reaction vial open to air. Gratifyingly, some of the C=C bond was found to be cleaved, and acetophenone (**2a**) was obtained in 18% isolated yield (Scheme 3). Like in other radical-mediated OCO methods, we also believed that the key intermediate was the dioxetane (**6**), which was formed from intermediate **5** by the abstraction^[26] and substitution of the thiyl radical. Although dioxetane **6** could not be directly observed since it spontaneously decomposed upon formation^[6,7] to give product **2a**, several observations were informative to confirm the proposed pathway: 1) The tertiary radical (**3**) from the thiyl addition underwent α -hydrogen abstraction to give trace amount of compound **4**, which was observed by GC-MS; 2) When the reaction was performed in the presence of methionine (1 equiv) and water as the trapping reagents for dioxetane,^[27] the formation of diol **8** was detected.

Scheme 3. Visible-light oxidative C=C bond cleavage catalyzed by bis(4-methoxyphenyl) disulfide

A set of experiments was performed to confirm the efficacy of disulfides as photo-precatalysts. In the absence of disulfide **S1**,

no ketone product was observed (Table 1, entry 1). The dark reaction in the presence of **S1**, either at ambient temperature (entry 2) or heated to 45 °C (entry 3), afforded no observable product. The reaction in the presence of molecular oxygen (1 bar) gave an elevated yield of 83% (Table 1, entry 4) compared to the reaction under air. We also examined other disulfides such as bis(phenyl), bis(*p*-tolyl), bis(*p*-chlorophenyl),^[28] and bis(2-thiophenyl) disulfides (**S2–S5**, entries 5–8), which all gave lower yields than **S1**. Inorganic compounds with S–S bond such as sodium metabisulfite (**S6**) were also examined, however, no ketone **2** was formed in 16 hours (entry 9).

Table 1. Exploring reaction conditions.

Entry	Catalyst	Oxidant	Light	T/°C	Yield% ^a
1	none	air	white LED	25	0
2	S1	air	dark	25	0
3	S1	air	dark	45	0
4	S1	O ₂	white LED	25	83
5	S2	O ₂	white LED	25	53
6	S3	O ₂	white LED	25	72
7	S4	O ₂	white LED	25	70
8	S5	O ₂	white LED	25	29
9	S6	O ₂	white LED	25	0

[a] Based on yields of isolated product.

With the optimal disulfide confirmed as **S1**, we set out to explore more olefinic substrates. At room temperature, a diverse set of aromatic olefins could be converted to corresponding ketones and aldehydes with 1 bar of O₂ and catalytic amount of **S1** (Table 2). The reaction with α -methylstyrene analogs (**1b–1d**) all afforded excellent yields of the ketone products (**2b–2d**). Benzophenone (**2e**) could be prepared from 1,1-diphenylethylene (**1e**) in 76% yield, which however required more catalyst (10 mol%). Styrene and its derivatives with *ortho*-, *meta*- and *para*-substituents (**1f–1i**) could all be converted into the aldehyde products in 70–80% yield. In general, the oxidation of 1,2-disubstituted olefins (**1j–1m**) also went smoothly and moderate to good yields were obtained, with the only exception of the reaction of (*Z*)- β -methylstyrene (**1k**), in which a part of the starting material either isomerized to the (*E*)-alkene (**1j**) or was epoxidized.

Table 2. Disulfide-catalyzed photo-oxidation of aromatic olefins.

Olefin $\xrightarrow[\text{white-LED, MeCN, 25 } ^\circ\text{C, 16 h}]{\text{S1 (5 mol\%), O}_2 \text{ (1 bar)}}$ Ketone / Aldehyde			
Olefin	Product and Yield ^a	Olefin	Product and Yield ^a
2b, 91%		2h, 75%
2c, 92% ^c		2i, 77%
2d, 87%		2j, 79% ^d
2e, 76% ^{b,c}		2k, 44% ^e
2f, 73% ^c		2l, 76%
2g, 75%		2m, 60%

[a] Based on yields of isolated product. [b] With 10 mol% catalyst. [c] Acetone as solvent. [d] 1,4-Dioxane as solvent. [e] Methanol as solvent.

It is commonly believed that the photolysis of most aromatic disulfides requires UV irradiation.^[13,15,16] In order to prove that the light from the LED light source was not able to generate the thiyl radical from the disulfide, we carried out two control experiments. Under white LED light, the disulfide-disulfide exchange between bis(4-methoxyphenyl) disulfide (**S1**) and dimethyl disulfide (**S7**) did not take place (Scheme 4). In contrast, the mixture disulfide formed with 9% yield in 1 hour with irradiation from a medium-pressure Hg lamp. The reason a dialkyl disulfide was chosen for the cross-over experiment was that the exchange between two aromatic disulfides can occur via a concerted mechanism without light.^[29–31] The photo-addition of disulfide to terminal alkyne under UV was first observed for dialkyl disulfide by Heiba and Dessau in 1960s.^[32] A recent example was reported by Ogawa,^[14] in which diphenyl disulfide could be trapped by 1-octyne with light from a medium-pressure Hg lamp. However, under LED irradiation, an equimolar mixture of 1-heptyne and diphenyl disulfide (**S2**) did not undergo any addition reaction. These results suggested that the S–S bond of common aromatic disulfides cannot be cleaved to give thiyl radicals with light from an LED lamp (Scheme 4).

Scheme 4. The control experiments

Thus, it is reasonable to assume that the olefin and disulfide have interactions that facilitate the S–S bond photolysis, with the olefin acting as a sensitizer. Following Szmant's procedure to confirm the thiol-olefin charge-transfer complex in the 1980s,^[21a] we carried out a set of NMR experiments to seek evidence of the disulfide-olefin complex. By analyzing a series of ¹H NMR of a fixed amount of disulfide **S1** mixed with increasing amounts of α -methylstyrene (**1a**), we found that the chemical shift of the disulfide's methoxy group distinctly drifted towards upfield, which indicated that the electron density on the disulfide had increased. This observation could be explained by the electron-donation from the olefin's conjugated π -system to the sulfur atom, based on the same observation and rationalization for the thiol-olefin system.^[18–21] The chemical shifts for the olefin remained largely unchanged. The slope of the curve decreased with the increasing relative concentration of olefin, indicating that the charge-transfer complex was forming towards saturation (Figure 1).

Figure 1. Correlation between the chemical shift of –OMe of **S1** and the relative olefin concentration.

In addition to experimental results, computational studies were also performed for the disulfide-olefin charge-transfer complex. The UV-Vis spectra^[33,34] of **S1** and the complex **S1-1a** were simulated by DFT calculation at the ω B97x-D/6-31G* level of theory, which was previously used for theoretical studies of the spectroscopic behavior of various disulfides.^[35] The energy and UV-Vis spectrum of **S1** were first calculated to confirm the accuracy of the method. The energy gap between HOMO (–7.83 eV) and LUMO (+0.59 eV) was calculated to be 8.42 eV (Figure 2). The calculated absorption of **S1** fell within the UV region (< 400 nm, Figure 3) and was in accord with the experimental spectrum (see the Supporting Information).

The structure of the disulfide-olefin complex (**S1-1a**) was proposed based on the results of NMR experiments that the electron density at the disulfide was increased, and also based on Fava^[18] and Szmant's^[20–21] models that the HOMO of the olefin preferably interacts with the LUMO of the thiol (here it is the LUMO of the disulfide). The complex's geometry was optimized based on the same DFT method (ω B97x-D/6-31G*) for calculating the energy of **S1**. The disulfide-olefin complex (**S1-1a**) displayed a reduced HOMO–LUMO gap of 7.31 eV

(HOMO = -6.89 eV, LUMO = $+0.42$ eV) as compared to that of the free disulfide **S1** (Figure 2). The reduced HOMO–LUMO gap might be attributed to the elevation of HOMO caused by the electron-donation from the C=C π -orbital to the sulfur (as graphically shown in Figure 2).^[21a] The calculated UV-Vis spectrum of the complex (**S1-1a**) showed that the range of absorption had extended to the visible region (400–430 nm) (Figure 3). Therefore, the olefin-activated disulfide would lead to a more feasible homolytic S–S bond dissociation under visible-light, and a subsequent thiyl addition to the C=C bond.

Figure 2. Modeling of the disulfide-olefin complex and energy levels by DFT calculation

Figure 3. The simulated UV-Vis spectra of **S1** and the disulfide-olefin complex (**S1-1a**)

In conclusion, we have developed a mild and non-metal catalyzed method for the aerobic oxidative cleavage the C=C bond under visible-light at room temperature. Bis(4-methoxyphenyl) disulfide was employed as photocatalyst, and typical monosubstituted as well as 1,1- and 1,2-disubstituted aromatic alkenes could be converted to corresponding aldehydes and ketones. Interestingly, we have discovered that the coordinating effect between thiols and olefins might also exist between certain disulfides and olefins. The unconventional homolysis of the aromatic S–S bond by visible-light was rationalized by the olefin-disulfide charge-transfer complex. Mechanistic details of this effect and more synthetic applications are currently being investigated in our lab.

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Keywords: Organocatalysis • Disulfide Catalyst • Olefin Oxidation • Visible-Light Photocatalysis • Donor-Acceptor Complex

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COMMUNICATION

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