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COMMUNICATION

Reusable Cobalt-Phthalocyanine in Water: Efficient Catalytic Aerobic Oxidative Coupling of Thiols to Construct S-N/S-S Bonds

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A new aerobic oxidative coupling of thiols in water to construct sulfenamides or disulfides was developed, utilizing cobalt(II)phthalocyanine-*tetra*-sodium sulfonate as the catalyst and O_2 as the oxidant. The mother liquor could be recycled up to 20 times with negligible loss of activity and only a minor decrease of product yield.

Organosulfur compounds have been vitally applied as synthetic intermediates and reagents in organic synthesis, pharmaceutical and biological science.[1, 2] For instance, organic compounds containing S-S bonds, defined as disulfides, are key motifs to stabilize proteins structures and responsible for their biological activities.[3-6] Furthermore, the unique structure and properties of S-N bonds in sulfenamides have found their utilization as functional groups in natural product synthesis and ubiquitous intermediates in the preparation of fine chemical products such as accelerators for rubber vulcanization in industry.[7-10] Conventional methods to achieve S-S bonds involve metal-catalyzed or metal-free oxidative coupling of thiols. There have been many reports about metal-free oxidation using hydrogen peroxide, azo reagents, halogen, sodium nitrite, or Burgess Reagent.[11-19] Metal-containing catalysts or oxidants, such as Al,[20] Cr,[21, 22] Mn,[23] Fe,[24] Co,[25] Cu,[26] Pb,[27] or Ce,[28] are typically used.[29] However, when it comes to sulfenamides, the transition-metal-catalyzed coupling of thiols with amines has not been well developed up to date, due to the difficulty to avoid disulfide as homocoupling product or the formation of an inactive metal-thiolate complex.[30-32] To solve these problems, various metal catalysts have been studied, and it turns out that the utilization of copper catalyst results in the formation of sulfenamides with good yields and selectivity.[32-34] Nevertheless, the shortcomings are apparent, including toxic waste, harsh reaction conditions (such as high temperature, long reaction hours, and risk of over-oxidation), extra additives or bases, and tedious work-up procedures. Therefore, the development of a novel and green catalytic method that can be carried out under mild conditions for the synthesis of sulfenamides and disulfides remains a challenge and is highly desired.

Over the past few decades, the sulfenamide accelerators have been the most prevalent in the industry. Among those, *tert*-butyl-2-benzothiazole sulfenamide (TBBS) stands out for its delayed action and faster curing rate.[35, 36] From the industrial, environmental, and biological prospects of view, we sought to exploit a new catalytic system for the synthesis of such compounds, by using molecular oxygen as the oxidant and water as the solvent. For green and sustainable chemistry, molecular oxygen has been considered as an ideal oxidant in organic synthesis due to its natural, cheap and environmentally abundant properties.[37-39] While some respectable achievements have been made, more efforts are still required for its practical application in the industrial production. Herein, we reported a reusable Co-catalyzed aerobic oxidative coupling of thiols to construct sulfur-nitrogen and sulfur-sulfur bonds in water.

Our initial attempt at the catalytic synthesis of sulfenamides explored the use of transition-metal complexes as the catalyst (Table 1). A sustainable catalyst should qualify two requirements: 1) slight solubility in the water and 2) good tolerance against amines and thiols. The latter was screened by slowly adding amine to the aqueous solution of a metal complex. Precipitation would be observed if catalyst poisoning occurs. Taking clues from this, a few transition metal complexes were suitable to screen the reaction of thiol with amine (Table 1, Entry 1-9).

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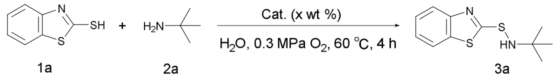
Table 1. Catalyst Screening.[a]



Entry	Catalyst	wt%	Yield (%)[b]
1	Na[Fe(EDTA)]	0.8	33
2	Na[Co(EDTA)]	0.8	59
3	Na_2[Cu(EDTA)]	0.8	68
4	Na_2[Mn(EDTA)]	0.8	7
5	Na_2[Ni(EDTA)]	0.8	trace
6	Co(phcy)$(COONa)_4$	0.8	76
7	Fe(phcy)$(COONa)_4$	0.8	trace
8	Cu(phcy)$(COONa)_4$	0.8	70
9	**Co(phcy)$(SO_3Na)_4$**	**0.8**	**95**
10	Co(phcy)$(SO_3Na)_4$	1.0	87
11	Co(phcy)$(SO_3Na)_4$	0.6	82
12	Co(phcy)$(SO_3Na)_4$	0.4	68
13	Co(phcy)$(SO_3Na)_4$	0.2	15
14	-	-	0

[a] Reaction conditions: **1a** (2 mmol), **2a** (10 mmol), catalyst, 10 mL H_2O, 0.3 MPa O_2, 60 °C, 4h. [b] Isolated yields.

All tested reactions were conducted with 2-mercaptobenzothiazole **1a** and *t*-butylamine **2a** in a reactor under 0.3 MPa O_2 at 60 °C for 4 hours. The desired product **3a**, TBBS, was predicted to precipitate out due to its low solubility in the solution. As expected, the reaction mixture was filtered once completed, and the precipitation was washed with water and collected as product. Initially, 0.8 wt% Na[Fe(EDTA)] was tested and **3a** was formed in 33% yield, fortunately (Entry 1). More metal-EDTA complexes were screened under the same catalyst loading. When Na[Co(EDTA)] and Na_2[Cu(EDTA)] were used as the catalysts, **3a** was produced in 59% and 68% yield, respectively (Entry 2, 3). However, when it came to Na_2[Mn(EDTA)] and Na_2[Ni(EDTA)], only trace amount of product was formed (Entry 4, 5). Apparently, the metal-EDTA complex with a copper or cobalt center had a higher catalytic ability, albeit in modest yields. Then, we changed the ligand to phthalocyanine-tetra-sodium carbonate. Compared with NaM(EDTA) (M = Co, or Cu), M(phcy)$(COONa)_4$(M = Cu or Co) showed stronger catalytic ability and led to higher yields (Entry 6, 8). Interestingly, only trace amount of product was collected when Fe(phcy)$(COONa)_4$ was adopted (Entry 7), illustrating certain ligand effect on the catalytic performance. A modified Co catalyst, Co(phcy)$(SO_3Na)_4$, successfully increased the yield to 95% (Entry 9). By varying the loading of Co(phcy)$(SO_3Na)_4$ from 0.2 wt% to 1 wt%, 0.8 wt% turned out to be the optimum amount (Entry 9-13). Notably, when the catalyst loading rose from 0.8 wt% to 1 wt%, the yield decreased. To understand this unanticipated reduction, we set eyes on the work-up procedure. When 1 wt% Co(phcy)$(SO_3Na)_4$ was applied, the product was slightly blue after filtration, indicating trace catalyst residue. Furthermore, it has been reported that Co(phcy)$(SO_3Na)_4$ intends to form oligomers in concentrated aqueous solution due to intermolecular π-π stacking, reducing its solubility and catalytic performance. In summary, even though higher yield could be achieved with higher catalyst loading, an upper limit exists. The control experiment, in which no catalyst was added, resulted in no product, confirming the necessity of Co(phcy)$(SO_3Na)_4$ in the catalytic cycle (Entry 14).

Table 2. Optimization of reaction conditions between **1a** and **2a**.[a]

Entry	T / °C	ΔP (O_2)/MPa	Ratio[b]	Yield (%)[c]
1	50	0.3	1:5	52
2	**60**	**0.3**	**1:5**	**95**
3	70	0.3	1:5	75
4	80	0.3	1:5	67
5	90	0.3	1:5	11
6	100	0.3	1:5	trace
7[d]	60	-	1:5	26
8	60	0.1	1:5	63
9	60	0.2	1:5	70
10	60	0.4	1:5	87
11	60	0.5	1:5	83
12	60	0.6	1:5	78
13	60	0.3	1:4	87
14	60	0.3	1:3	trace
15	60	0.3	1:2	trace
16	60	0.3	1:1	trace

[a] Reaction conditions: **1a** (2 mmol), **2a** (10 mmol), Co(phcy)$(SO_3Na)_4$(0.8 wt%), H_2O, 0.3 MPa O_2, 4 h. [b] Ratio of amine against thiol. [c] Isolated yields. [d] Air atmosphere.

In the further optimization of the reaction conditions, we evaluated temperature, O_2 pressure, and the ratio of **2a** against **1a** (Table 2). The temperature parameter study was carried out in six various reaction temperatures (Entry 1-6). As the maximum yield of 95% was obtained at 60 °C, either higher or lower temperature decreased the yield of **3a**. Furthermore, the effect of O_2 pressure was studied by varying the pressure of O_2 from 0.2 to 0.6 MPa. There was an increase of the yield with the O_2 pressure up to 0.3 MPa, and after that, the yield decreased. When the reaction was conducted in air, the product was obtained only in 26% yield (Entry 7). It is known that the combination of O_2 with the catalytic metal center is affected by O_2 pressure. Thus, it is reasonable that the yield increased beyond 0.3 MPa O_2 (Entry 2, 7-9). However, lower yield was observed once the O_2 pressure is further increased, illustrating lower selectivity of the desired product (Entry 10-12). The ratio of **2a** against **1a** was examined in five different values (Entry 2, 13-16), and the raising ratio of **2a** increased the yield evidently. When only one equivalent of *t*-butylamine was added to the reaction mixture, the well-suspended **1a** turned into a

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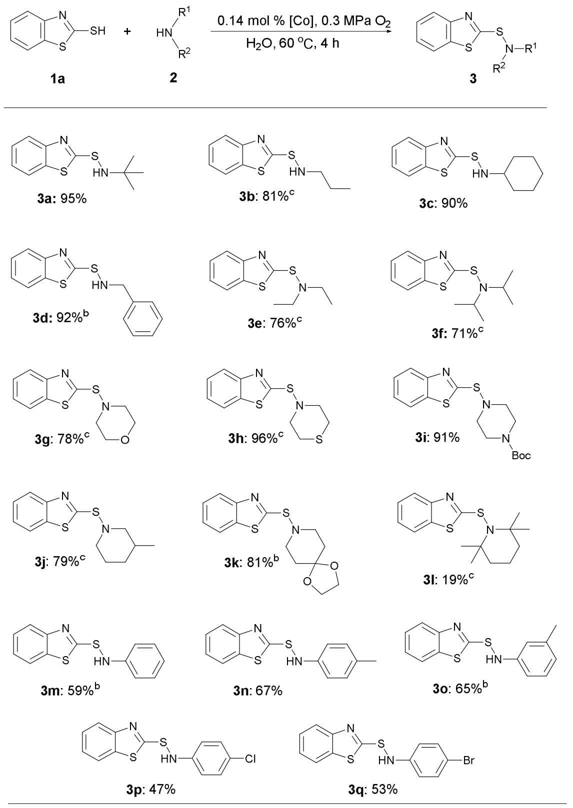
glutinous mixture, which should be the neutral onium salt and caused inefficient stirring. Moreover，**1a** favored its homocoupling with a low ratio of amine. Following its increasing equivalents, **2a** started to serve as an organic co-solvent and promote the diffusion of **1a** into water. Since we were aiming at a catalytic reaction in water and 95% yield was acceptable, it was unnecessary to increase the ratio higher than 1:5.

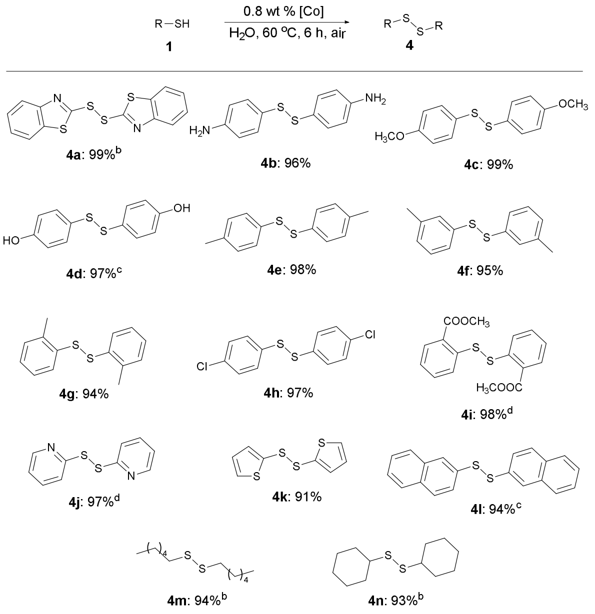
Table 3. The scope of amines.[a]



[a] Reaction conditions: **1** (2 mmol), **2** (10 mmol), Co(phcy)$(SO_3Na)_4$ (0.8 wt%), 0.3 MPa O_2, 10 mL H_2O, 60 ℃, 4 h. [b] 20 mmol amine; [c] 40 mmol amine.

With the optimal reaction conditions in hand, the substrate scopes of **1a** were explored with a large variety of amines (Table 3). In general, all alkyl amines and aryl amines were well tolerated and furnished the desired sulfenamides in modest to excellent yields. Primary and secondary alkyl amines gave target products in relatively higher yields as compared to aryl amines. The use of primary alkyl amines as a reaction partner provided **3a-d** in 81-95% yield. Secondary alkyl amines were able to give sulfenamides **3e-l** in good to excellent yields as well. Moreover, cyclic secondary amines afforded sulfenamides **3g-k** in higher yields, comparing with other secondary alkyl amines (**2e, f**). This might be due to higher steric hindrance caused by the two flexible alkyl chains on the amines (**2e, f**). Higher equivalents of those substrates (**2e, f**) are also required. This hypothesis was further confirmed by the employment of 2,2,6,6-tetramethylpiperidine **2l** as a reaction partner, which led to **3l** in as low as 19% yield. Aniline **2m** and its derivatives **2n-o** bearing methyl group at para- or meta-position on the benzene ring resulted in the desired sulfenamides **3m-o** in 59-67% yields. 4-Chloroanilne and 4-bromoaniline furnished products **3p** and **3q** in 47% and 53% yields, respectively. Conclusively, aromatic amines bearing electron-withdrawing substituents led to lower yields. Except for **1a**, we tried other thiols, for instance, substituted phenylthiol. Unfortunately, none of those worked. Despite this defect, our work shows great potential in industrial production of rubber vulcanization accelerators since the work-up procedure is operationally efficient.

Table 4. Synthesis of Symmetric Disulfides.



[a] Reaction conditions: **1** (2 mmol), Co(phcy)$(SO_3Na)_4$ (0.8 wt%), 10 mL H_2O, 60°C, air. [b] 0.3 MPa O_2, 4 h. [c] t = 9 h. [d] t = 12 h.

Then we took an advantage of this novel and environmentally friendly Co-catalyzed system for the homocoupling of thiols to construct symmetric disulfides (Table 4). The homocoupling was initially tested on **1a** as well. Instead of the optimal condition, a modified reaction condition was used, in which the reaction time was extended to 6 h and the O_2 atmosphere was replaced by air. Excitingly, 2,2-dibenzothiazole disulfide **4a** was obtained in 99% yield. To screen the generality of this method, a series of alkyl and aryl thiols were tested and well tolerated. Substituted thiophenols bearing electron-donating groups (**1b-g**), such as amino, methoxyl, hydroxyl, or methyl group, and electron withdrawing groups (**1h-i**), such as chloro or methoxycarbonyl group, gave all desired disulfides **4b-i** in excellent yields. In spite of the electronic effect, thiophenols with methyl group in the ortho-, meta- or para-position showed no significant difference on the yields, either.

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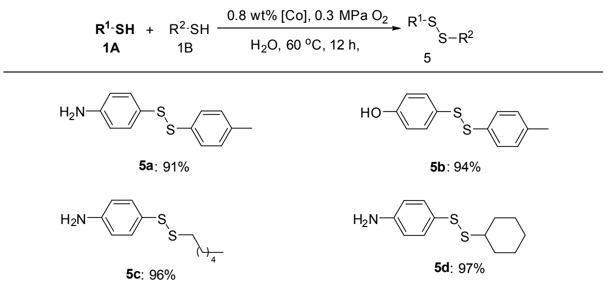
Comparing with the 98% yield of **4e**, the slightly lower yield of **4g** might be due to the steric effect of the methyl group on ortho-position. Heteroaromatic thiols, such as 2-mercaptopyridine **1j** and 2-thiophenethiol **1k**, were oxidized to disulfides **4j** and **4k** in 97% and 91% yields, respectively. Naphthyldisulfide **4l** with extended π-framework was synthesized in 94% yield. Aliphatic thiols led to desired products, **4m** and **4n**, in 94% and 93% yield, respectively. Conclusively, this oxidative coupling of thiols in the aqueous phase is highly versatile and efficient for the synthesis of a large variety of symmetric disulfides.

We were curious to continue our investigation with the synthesis of asymmetric disulfides. It came to the determination that the crosscoupling favors electron-efficient aromatic thiols (Table 5). Reactions with mixture of two aromatic thiols led to the formation of target asymmetric disulfides (**5a** and **5b**) in relatively high yields (91% to 94%). Reactions between aromatic and aliphatic thiols led to the formation of the target disulfides (**5c** and **5d**) in excellent yields (96% to 97%).

Table 5. Synthesis of Asymmetric Disulfides.



[a] Reaction conditions: **1A** (1mmol), **1B** (5mmol), $Co(phcy)(SO_3Na)_4$(0.8 wt%, calculated with **1A**), 5 mL H_2O, 60 °C, 12 h, 0.3 MPa O_2.

Since it was our purpose to design a convenient and clean method for industrial manufacturing, a large-scale testing was performed under the optimal reaction condition (Figure 1). Once the reaction completed, the reaction mixture was filtered, and the solid was washed by H_2O to give pure product in 85% yield. Further extraction of the aqueous layer furnished another portion in 6%. Such easily scaled-up reaction guaranteed the promising application of our methodology in chemical manufacturing and commercialization. More importantly, the catalyst and excess amine remain in the aqueous phase after the desired product is easily collected through filtration. This strategy was expected to accomplish the comprehensive circulation of mother liquor. Thus, we performed the recovery of the mother liquor. It's worth noting that the mother liquor could be recycled up to 20 times with almost comparable reactivity and only a minor decrease of yield (Figure 1). Hence, $Co(phcy)(SO_3Na)_4$ in aqueous phase is proved to be an efficient catalytic system for the construction of S-N/S-S bonds.

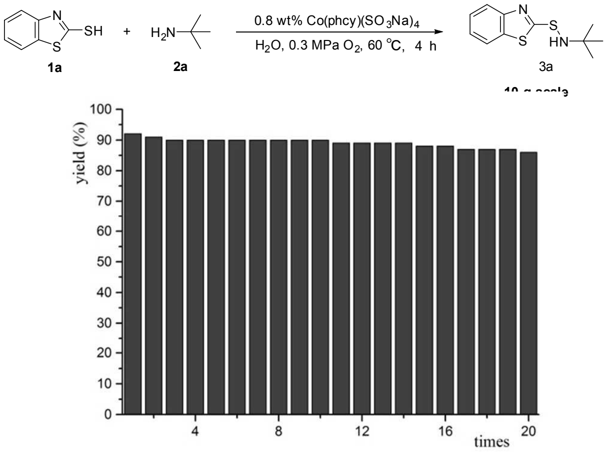
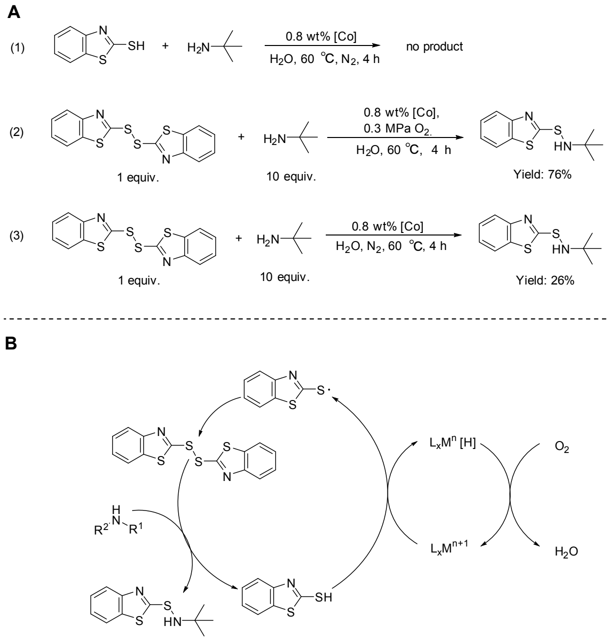


Figure 1. The circulation of the mother liquor.

Scheme 1. Experimental Evidence and Proposed Mechanism.



To gain some insights into the reaction mechanism of S-N bond formation, a few experiments were carried out. As mentioned (Table 1, Entry 14), no reaction of thiol with amine was observed in the absence of Co catalyst. The elimination of O_2 from the optimal condition led to no product, either (Scheme 1A, Reaction 1). Preliminary results are consistent with previous studies,[40-42] suggesting the formation of disulfide as homocoupling product is a key step in the catalytic cycle. Then, we replaced 1,2-bis(benzo[d]thiazol-2-yl)disulfane **4a** with **1a** to react with *t*-butylamine **2a** under the optimal reaction conditions (Schem 1A, Reaction 2). TBBS **3a** was produced in a moderate yield (76%), which is lower than that of the

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reaction between **1a** and **2a**. Since amine was observed to serve as a co-solvent and showed significant effect on the reaction, the relatively lower solubility of **4a** as compared to **1a** should be responsible for the decreasing yield. To sum up, **4a** serves as an intermediate in the catalytic cycle and is significant to activate N-H bond of amines. A control experiment of **4a** with **2a** under N_2 was carried out to give TBBS in 26% yield (Scheme 1A, Reaction 3), stating that O_2 participates in the transformation of disulfide intermediate into sulfenamide.

On the basis of above observations, the present Co-catalyzed aerobic oxidative reaction mechanism to construct S-N bond is proposed as shown in Scheme 1B. Initially, the interaction of O_2 with the Co(II) center results in the formation of Co (III) complex.[43-46] The reduction of Co(III) complex by thiols regenerates the catalyst and gives the thiyl radical. The homocoupling of two thiyl radicals leads to disulfide as an intermediate. The reaction of disulfide with amine furnishes the desired sulfenamide and releases a thiol molecule to rejoin the catalytic cycle.

Conclusions

In conclusion, we successfully developed a highly efficient and versatile methodology to construct S-N/S-S bond. The water media under O2 atmosphere, in which cobalt(II)phthalocyanine-tetra-sodium sulfonate was adopt as the catalyst, turned out to be a straightforward and environment-friendly catalytic system for the oxidative coupling of thiols under mild condition. After the reaction, the catalyst within the solution can be easily recovered via filtration and reused without any particular treatment. Notably, the circulation of the mother liquor was conducted up to 20 times while the yield remains commensurate, providing a new prospect for commercial manufacturing of disulfides and sulfenamines in a much greener and economical way.

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