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Reduction of sulfoxides and pyridine-*N*-oxides over iron powder with water as hydrogen source promoted by carbon dioxide

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A green process was developed for efficient reduction of sulfoxides and pyridine-*N*-oxides using the iron powder in the presence of H₂O–CO₂ to sulfides and pyridines, respectively. Notably, H₂O is employed as the terminal hydrogen source, and CO₂ could enhance hydrogen generation through *in situ* formation of carbonic acid. Thus carbonic acid offers simple neutralization by depressurizing CO₂ and the system can eliminate unwanted byproducts. The high generality and chemo-selectivity of this protocol were demonstrated by the scope of substrates, in which chlorine, vinyl group and benzene ring can be tolerated.

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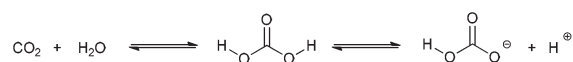
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Introduction

Carbon dioxide, as one of the main greenhouse gases, is gaining increasing concern from both academia and governmental agencies all over the world.¹ Therefore, controlling CO₂ emission and further reducing its accumulation is an urgent and challenging research topic. In this context, CO₂ chemistry based on its capture and utilization deserves much attention and great efforts from the scientific community and industrial sectors.^{2–7} On the other hand, CO₂ as an abundant and readily available C₁ resource has also shown significant potential and advantage in synthetic organic chemistry for production of value-added chemicals.^{8–12} Besides profound achievements in chemical fixation of CO₂, various feasible uses of CO₂ have been widely proposed, such as a sound reaction medium for green processes,¹³ Lewis acid catalyst and/or promoter,¹⁴ and tunable reagent for controlling chemical selectivity,¹⁵ providing feature advantages from the viewpoint of green chemistry.

Meanwhile, acids are the most commonly used catalysts both in academic research and industrial application, but such processes are generally accompanied by the disadvantage of requiring postreaction neutralization and salt disposal, which would cause severe environmental concerns.¹⁶ Notably, the reversible reaction of CO₂ with H₂O to form carbonic acid is well investigated, leading to a temporary *in situ* generated proton species with pH values as low as 3 (Scheme 1).¹⁷ Such a CO₂–H₂O system represents environmentally benign features not only because both H₂O and CO₂ are non-toxic, renewable



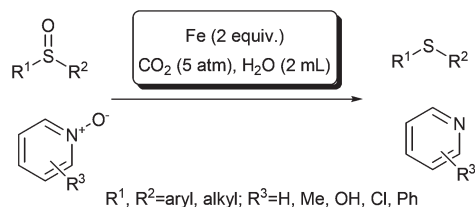
Scheme 1 Formation of carbonic acid from CO₂ and H₂O.

and easily available, but also due to its self-neutralization characteristic upon depressurization of CO₂ after reaction, which results in simple post-processing and no waste disposal.¹⁸ Such self-neutralizing *in situ* acid from CO₂–H₂O has been applied in acid catalysis with improved economics as well.^{18–23} In addition, the application of *in situ* carbonic acid has been lately extended to the selective reduction of aldehydes,²⁴ imines²⁵ and nitroarenes^{26–28} over metallic zinc or iron with H₂O as the terminal hydrogen source. Although there may be some limitations due to low solubility for organic reactants and incompatibility with water-sensitive compounds,^{27,29} the reversible system comprising CO₂–H₂O could be of great significance as an environmentally benign and promising tool for reductive transformations.

The reduction, *i.e.* deoxygenation, of sulfoxides^{30–34} and pyridine-*N*-oxides^{35–39} to the corresponding sulfides and pyridines is an important synthetic route that has found considerable utility in the field of organic synthesis and biological chemistry.^{40–51} Sulfoxides, mainly as chiral auxiliaries frequently employed in asymmetric synthesis,⁴¹ demand enduring efforts for the development of efficient methods to reduce the S=O moiety to the sulfides when their presence is no longer required after the chiral induction.⁴⁰ Likewise, pyridine-*N*-oxides, which could serve as temporary directing groups to alter the reactivity towards electrophilic substitution^{40,41} and C–H activation⁵² of aromatics, also require easy removal after completing their functions. Consequently, a great number of synthetic methodologies have been delivered for the purpose

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Scheme 2 Reduction of sulfoxides and pyridine-*N*-oxides by Fe powder in CO₂-H₂O system.

of reduction universality and convenience, whereas most of which suffer from disadvantages either induced by tedious work-up procedures with reagents that are not readily available and/or harsh conditions that restrict compatibility of functional groups, hence leading to environmental and practical operation problems. Therefore, it is still desirable to develop easily accessible reaction conditions with operationally simple procedures for such reduction. We herein would like to apply the self-neutralizing acid that forms *in situ* from CO₂ and H₂O to the reduction of sulfoxides and pyridine-*N*-oxides with facilitated reaction post-processing (Scheme 2). Various sulfides and pyridines were obtained in high yield and chemo-selectivity by using cheap, non-toxic, widely available and easily handled iron powder as the reductant.

Results and discussion

Initially, the reduction of diphenyl sulfoxide by metallic Fe powder in CO₂-H₂O system was studied as the model reaction to explore the influence of various reaction parameters. The reduction was performed in a 50 mL stainless steel autoclave equipped with an inner glass tube under CO₂ pressure. We found that diphenyl sulfoxide reacted smoothly in 2 mL of H₂O containing 2 equivalent of Fe powder under 8 MPa of CO₂, giving 89% yield of diphenyl sulfide (entry 1, Table 1). Several control experiments were performed to prove the synergistic effect between the reductant and carbonic acid formed *in situ* from CO₂ and H₂O. The reaction barely proceeded in the absence of either Fe powder or CO₂ (entries 2 and 3). An appropriate reaction temperature was also amenable for better productivity (entries 1 vs. 4 and 5). Such results prompted us to test other cheap and widely available metallic reductants commonly used in organic transformations. As listed in Table 1, a variety of reducing metals were examined, while only Zn showed a moderate reactivity, demonstrating that Fe is one of the most efficient reductants in the present reversible CO₂-H₂O system.

With the effective reductant in hand, we consequently turned our attention to exploring the effects of the reaction parameters. The results are summarized in Table 2. As illustrated in the literature, increasing CO₂ pressure certainly has a positive effect on the acidity of the reversible CO₂-H₂O biphasic system;⁵³⁻⁵⁵ too low CO₂ concentration would cause insufficient formation of carbonic acid and thus result in a deficient

Table 1 Reduction of diphenyl sulfoxide in CO₂-H₂O promoted by various metallic reductants^a

Entry	Reductant (mmol)	T (°C)	P _{CO₂} (MPa)	Yield ^b (%)
1	Fe (2)	80	8	89
2	—	80	8	—
3	Fe (2)	80	—	5
4	Fe (2)	60	8	50
5	Fe (2)	100	8	76
6	Zn (2)	80	8	56
7	Sn (2)	80	8	Trace
8	Mg (2)	80	8	Trace
9	Cu (2)	80	8	Trace
10	Al (2)	80	8	Trace
11	Mn (2)	80	8	Trace

^a Reaction conditions: diphenyl sulfoxide (1 mmol, 202.3 mg), H₂O (2 mL), 80 °C, 10 h. ^b Determined by GC with biphenyl as the internal standard.

Table 2 Optimization of various reaction parameters^a

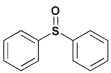
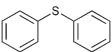
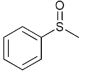

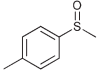

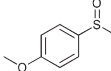

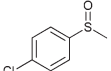

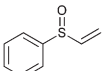

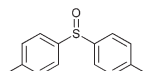
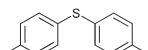
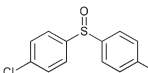
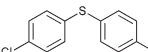
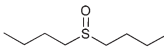
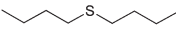


Entry	Fe (mmol)	H ₂ O (mL)	P _{CO₂} (MPa)	Yield ^b (%)
1	2	2	8	89
2	2	2	4	>99
3	2	2	1	97
4	2	2	0.5	95
5	2	2	0.2	34
6	2	2	12	52
7	2	1.5	0.5	78
8	1.5	2	0.5	67
9 ^c	2	2	0.5	89

^a Reaction conditions: diphenyl sulfoxide (1 mmol, 202.3 mg), H₂O (2 mL), 80 °C, 10 h. ^b Determined by GC with biphenyl as internal standard. ^c 5 h.

proton concentration. We found that lowering CO₂ pressure in the present procedure would contrarily enhance the reduction to be nearly quantitative (entries 1 to 3), and the high reductive efficiency of metallic Fe within the carbonic acid formed *in situ* would be definitely unfolded by the introduction of only 5 atm of CO₂, which is just enough for a considerable reaction outcome, making the protocol much more convenient and practical (entry 4). However, the reduction was observed to be sluggish under higher pressure, possibly due to the dilution effect of dense CO₂ (entry 6). Meanwhile, apart from the influence of CO₂ presence, H₂O as the actual proton donor could also play a crucial role in the formation of carbonic acid, and hence could reasonably have a significant impact on the reductive deoxygenation. Reducing the water amount to 1.5 mL led to a detrimental effect on the reaction (entries 7 vs. 2). Furthermore, decreasing the amount of reductant as well as shortening the reaction time were also revealed to be infeasible, leading to a drop-off of sulfide yield (entries 8 and 9).

The feasibility of this methodology was then evaluated by submitting the reduction to a broad range of sulfoxide-type substrates under typical reaction conditions. As shown in

Table 3 Fe-promoted reduction of sulfoxides in CO₂-H₂O system^a















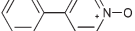
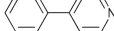


Entry	Substrate	Product	Yield ^b (%)
1			95 (91) ^c
2			>99
3			98
4			98 (77) ^c
5			98 (85) ^c
6			78
7			93 (87) ^c
8 ^d			78 (67) ^c
9 ^e			79
10			75

^a Reaction conditions: sulfoxide (1 mmol), Fe powder (2 mmol, 111.7 mg), CO₂ (0.5 MPa), H₂O (2 mL), 80 °C, 10 h. ^b Determined by GC. ^c Isolated yield. ^d Fe powder (4 mmol, 223.4 mg), CO₂ (2 MPa). ^e Fe powder (4 mmol, 223.4 mg), 100 °C.

Table 3, a variety of diaryl, dialkyl, alkyl aryl and vinyl aryl sulfoxides reacted smoothly, providing the corresponding sulfides in excellent yields. Substrates with either electron-releasing or electron-withdrawing substituents on the aromatic ring were all applicable for the reduction with no obvious preference on the reactivity (entries 3 to 5, 7 and 8). Notably, the present reduction system could display a preference towards the deoxygenation of the S=O moiety in high chemo-selectivity, since no dehalogenation or reduction of vinyl group was detected (entries 5, 6 and 8).

A rational investigation was further performed to extend the Fe(0)-promoted reduction to pyridine *N*-oxides aiming to explore its generality in deoxygenative transformation. The results are listed in Table 4. To our delight, nearly quantitative yield of pyridine was obtained after the introduction of unsubstituted pyridine *N*-oxide into the optimal reductive conditions employed in Table 3, except for a slightly elevated temperature (entry 1, Table 4). Again, the presence of CO₂ was clearly demonstrated to be indispensable, as almost no reaction happened without the participation of CO₂ (entry 2). Due to the compatibility with the wide range of functional groups clarified in the reduction of sulfoxides (Table 3), it is seems

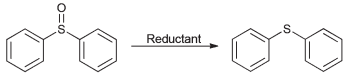
Table 4 Fe-promoted reduction of pyridine-*N*-oxides in CO₂-H₂O system^a

Entry	Substrate	Product	Yield ^b (%)
1			>99
2 ^c			Trace
3 ^d			73
4			(95) ^e
5			(>99) ^e
6 ^f			48
7			(90) ^e
8			(97) ^e
9 ^g			>99

^a Reaction conditions: pyridine-*N*-oxides (1 mmol), Fe powder (2 mmol, 111.7 mg), H₂O (2 mL), 100 °C, 10 h. ^b Determined by GC with biphenyl as internal standard. ^c Without CO₂. ^d Fe powder (4 mmol, 223.4 mg). ^e Isolated yield. ^f H₂O (1.5 mL), Fe powder (3 mmol, 167.5 mg). ^g CO₂ (2 MPa).

possible that such a system could also be suitable for the reduction of other pyridine *N*-oxides. Indeed, reactions of a series of pyridine-*N*-oxides bearing alkyl, aryl, methoxyl, hydroxyl and chloride substituents as well as morpholine-*N*-oxide selectively afforded the deoxygenated products in moderate to excellent yields (entries 3 to 9).

Finally, a preliminary investigation on the reaction pathway was carried out to certify the rational role of CO₂ and metallic Fe in the present deoxygenative protocol. As illustrated in Table 1, the conversion of diphenyl sulfoxide was enhanced by the introduction of CO₂, which could possibly be attributed to the increase of proton concentration as a result of the formation of carbonic acid. Such a hypothesis was confirmed by the quantitative yield of diphenyl sulfide after adding aqueous HCl to the reaction instead of CO₂ (entries 2 vs. 1, Table 5). Then the reaction vessel was injected with gaseous hydrogen (0.5 MPa) in the absence of CO₂, and a comparable result can also be attained (entry 3), which could give rise to the inference that hydrogen derived from the protons of the carbonic acid formed *in situ* by metallic Fe is the actual deoxygenation species. Furthermore, besides the formation of hydrogen, metallic Fe is also supposed to promote the oxygen transfer from the substrate to the hydric acceptor. Although the detailed mechanism is not yet clear, such a process could be implicated

Table 5 Mechanistic investigation of Fe-promoted reduction of sulfoxides in CO₂-H₂O system^a


Entry	Fe (mmol)	Additive	H ₂ (MPa)	P _{CO₂} (MPa)	H ₂ O (mL)	Yield ^b (%)
1	2	—	—	0.5	2	95
2 ^c	2	Aq. HCl	—	—	—	97
3	2	—	0.5	—	2	90
4	—	—	0.5	—	2	Trace
5 ^d	—	Fe ₂ O ₃	0.5	—	2	Trace
6 ^e	—	Fe ₃ O ₄	0.5	—	2	Trace

^a Reaction conditions: diphenyl sulfoxide (1 mmol, 202.3 mg), 80 °C, 10 h. ^b Determined by GC with biphenyl as internal standard. ^c Aq. HCl (4 M, 2 mL). ^d Fe₂O₃ (1 mmol, 159.7 mg). ^e Fe₃O₄ (1 mmol, 231.5 mg).

by the prohibited reduction in a hydric environment without metallic Fe (entry 4) or with Fe₂O₃/Fe₃O₄ instead of Fe (entries 5 and 6). Based on the aforementioned studies, the plausible mechanism is thought to occur in two steps: (i) the formation of hydrogen by the reaction of metallic Fe and the carbonic acid formed *in situ* from CO₂ and H₂O; (ii) the deoxygenation of the sulfoxide or pyridine-*N*-oxide with hydrogen mediated by the Fe species.

Conclusions

In summary, we have developed a green process for the reduction of various sulfoxides and pyridine-*N*-oxides by Fe powder within the reversible CO₂-H₂O system based on the understanding of *in situ* acid catalysis induced by CO₂, which could be inherently neutralized by ready removal of CO₂, thus resulting in simple neutralization and no waste disposal. Herein, H₂O would act as the terminal hydrogen source, while CO₂ plays an essential role to enhance the hydrogen production. Such a highly flexible and chemo-selective reduction system affords the corresponding sulfides and pyridines with other reducible substituents intact in good to excellent yields without any acid additives or organic solvents. Accordingly, those findings disclosed in the present study could provide an ecologically safe, cost-effective and industrially feasible route to sulfides and pyridines, and would also open up the possibility of turning captured CO₂ from waste into a potential resource as a reaction medium and promoter, which would render its wide applications in green chemical processes.

Experimental

Materials

p-Tolyl methyl sulfoxide, 4-methoxyphenyl methyl sulfoxide, *p*-chlorophenyl methyl sulfoxide, phenyl vinyl sulfoxide were prepared according to the published procedures.^{56,57} The rest of substrates were purchased from Alfa Aesar China Co., Ltd

and Aladdin Reagent Inc. Distilled water and all the other reagents were obtained commercially from Tianjin Guangfu Fine Chemical Research Institute and used without further purification.

Experimental methods

¹H NMR spectra were recorded on a Bruker 400 spectrometer in CDCl₃ or CD₃OD, and CDCl₃ (7.26 ppm) or CD₃OD (4.87 ppm) was used as the internal reference; ¹³C NMR spectra were recorded at 100.6 MHz in CDCl₃ or CD₃OD, and CDCl₃ (77.0 ppm) or CD₃OD (49.0 ppm) was used as internal reference. GC analysis were performed on a Shimadzu GC-2014 equipped with a capillary column (RTX-Wax 30 m × 0.25 μm or RTX-17 30 m × 0.25 μm) using a flame ionization detector by comparison with the retention time of authentic samples. GC-MS data were collected on Finnigan HP G1800 A.

General procedure for the reduction of sulfoxides

A mixture of sulfoxides (1 mmol), Fe (2 mmol, 111.7 mg) and H₂O (2 mL) was placed in a 50 mL stainless steel autoclave equipped with an inner glass tube at room temperature. The vessel was sealed and CO₂ was subsequently introduced into the autoclave. The system was heated under the predetermined reaction temperature for 25 min to reach the equilibration, the final pressure then was adjusted to the desired pressure by introducing the correct amount of CO₂. After the reaction was finished, the vessel was cooled in an ice-bath and the pressure was released slowly to atmospheric pressure. The products were diluted with ethyl acetate and analyzed by GC. The residue was purified by column chromatography on silica gel (200–300 mesh, eluting with *n*-hexane) to afford the desired product. The isolated products were further identified with NMR spectra and GC-MS, which are consistent with those reported in the literature.

General procedure for the reduction of pyridine-*N*-oxides

A mixture of pyridine-*N*-oxides (1 mmol), Fe (2 mmol, 111.7 mg) and H₂O (2 mL) was placed in a 50 mL stainless steel autoclave equipped with an inner glass tube at room temperature. The vessel was sealed and CO₂ was subsequently introduced into the autoclave. The system was heated under the predetermined reaction temperature for 25 min to reach the equilibration, then the final pressure was adjusted to the desired pressure by introducing the correct amount of CO₂. After the reaction was finished, the vessel was cooled with an ice-bath and the pressure was released slowly to atmospheric pressure. The products were diluted with diethyl ether or acetone and analyzed by GC. The residue was purified by column chromatography on silica gel (200–300 mesh, eluting with *n*-hexane and ethyl acetate or methanol) to afford the desired product. The isolated products were further identified with NMR spectra and GC-MS, which were consistent with those reported in the literature.

Characterization data for representative products

Diphenyl sulfide.³² The product was obtained as a pale yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ: 7.39 (d, *J* = 7.4 Hz, 4 H), 7.34 (dd, *J* = 9.9, *J* = 4.8 Hz, 4 H), 7.28 (dd, *J* = 7.6, *J* = 5.1 Hz, 2 H). ¹³C NMR (100.6 MHz, CDCl₃) δ: 135.86, 131.10, 129.25, 127.10. EI-MS, *m/z* (%): 186 (100) [M⁺].

Phenyl methyl sulfide.³² The product was obtained as a pale yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ: 7.32–7.20 (m, 4 H), 7.17–7.07 (m, 1 H), 2.47 (s, 3 H). ¹³C NMR (100.6 MHz, CDCl₃) δ: 138.40, 128.80, 126.61, 125.00, 15.83. EI-MS, *m/z* (%): 124 (100) [M⁺].

Pyridine.⁵⁸ The product was obtained as a pale yellow liquid. ¹H NMR (400 MHz, CDCl₃) δ: 8.67–8.55 (m, 2 H), 7.66 (dd, *J* = 10.7, *J* = 4.6 Hz, 1 H), 7.34–7.22 (m, 2 H). ¹³C NMR (100.6 MHz, CDCl₃) δ: 149.86, 135.93, 123.72. EI-MS, *m/z* (%): 88 (74) [M⁺].

4-Phenylpyridine.⁵⁹ The product was obtained as a white solid. ¹H NMR (400 MHz, CDCl₃) δ: 8.67 (d, *J* = 5.3 Hz, 2 H), 7.65 (d, *J* = 7.2 Hz, 2 H), 7.59–7.40 (m, 5 H). ¹³C NMR (100.6 MHz, CDCl₃) δ: 150.19, 148.47, 138.11, 129.13, 127.01, 121.67. EI-MS, *m/z* (%): 155 (100) [M⁺].

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