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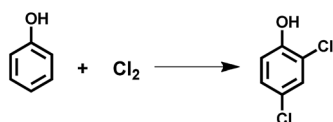
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Selective water-based oxychlorination of phenol with hydrogen peroxide catalyzed by manganous sulfate†

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Chlorination of phenols is a key synthetic method because chloro-substituted phenols are essential materials in the synthesis of herbicides, pharmaceuticals, insecticides, dyes, etc.^{1,2} Among the various chloro-substituted phenols, main products include *p*-chlorophenol, *o*-chlorophenol, 2,4-dichlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol, which belong to a group named “high chlorophenols”.³ In this group, 2,4-dichlorophenol is the most important material since it is an intermediate for 2,4-dichlorophenoxyacetic acid, a herbicide which is widely used in crops, rice and other massive cereals. Traditional methods for the synthesis of 2,4-dichlorophenol are all in olefin electrophilic aromatic chlorination of phenol with chlorine gas (Scheme 1).^{3–5} However, the utilization of chlorine atoms in these processes is quite low, nearly half of the chlorine is released as waste gas, which results in a waste of material and environmental hazards.



Scheme 1 Electrophilic aromatic chlorination of phenol with chlorine gas.

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An alternative solution is oxidative chlorination, i.e. oxychlorination, which uses chloride anions as a chlorine source in the presence of an oxidant (Scheme 2).^{6–12} In these systems, chloride anions are oxidized to chlorine by the oxidant and subsequently incorporated into the products. In general, chlorinating agents, such as sulfuric chloride,^{4,13} *N*-chlorosuccinimide,^{11,12} copper chloride,^{14–17} diamine perchloride¹ and *p*-toluenesulfonic chloride,¹ are used as chlorine sources, and reagents like sulfuric acid,¹ perchloric acid,^{12,20} lithium diisopropylamide,¹ dimethyl sulfoxide,²¹ etc.²² are employed as oxidants. While the utilization of chlorine atoms in oxychlorination is remarkably increased compared to only half in traditional methods, further research is still required to be cheaper and environmentally friendly reagents.

Compared to the most studies focused on the synthesis of monochloro-substituted phenols,^{4,23–27} the oxychlorination of phenols to 2,4-dichlorophenols is rather limited so far.^{3,20,2} For example, Gusevskaya *et al.* reported a method for aerobic oxychlorination of phenols over a CuCl_2 catalyst, in which metal chlorides were used as chlorinating agents.^{30,31} Feng *et al.* found a microaerobic method for aerobic oxychlorination of phenols catalyzed by CuCl_2 in hydrochloric acid as a chlorine source.²³ However, these methods are employed for the synthesis of *p*-chlorophenols. Notably, Ranjansam *et al.* developed a promising method for the oxychlorination/oxybromination of aromatics including phenols over copper phthalocyanines



Scheme 2 Oxychlorination of phenol with hydrogen peroxide catalyzed by manganous sulfate.



On the other hand, the use of water as a solvent is particularly attractive because: (1) water is cheaper than VOC solvents; (2) the risk of explosions using a water-based system is much lower than for systems containing VOCs; (3) 2,4-dichlorophenol is almost insoluble in water, and hence the product can be obtained by simple phase separation, which is convenient in application. However, this is a challenging topic, especially since catalytic methods for 2,4-dichlorophenol with high activity and selectivity have not been reported previously.

Herein, we present an efficient manganese(II) sulfite-catalyzed chlorination of phenol in water using hydrogen peroxide as the chlorinating system $\text{HCl}/\text{H}_2\text{O}_2$ (Scheme 4). Complete conversion of phenol and high selectivity for 2,4-dichlorophenol are both achieved under mild conditions. To the best of our knowledge, this is the first report on selective water-based chlorination of phenol in 2,4-dichlorophenol in the liquid phase under VOC-free conditions.

In a typical reaction, phenol (**1**) and a catalyst were added into water in a glass flask, and gaseous HCl was introduced to form a homogeneous solution. Then, 30% of an aqueous solution of H_2O_2 was added to start the reaction. In the initial study, the molar ratio of $\text{HCl}:\text{H}_2\text{O}_2:\mathbf{1}$ was 7.1:1.9:1 as used to screen the catalysts, and the results are shown in Table 1. In the absence of H_2O_2 , no reaction occurred even with a prolonged time (Table 1, run 1). When H_2O_2 was added in the absence of a catalyst, conversion of **1** reached 69% with a total yield of 67%, the products were composed of <1% of 2,4-dichlorophenol (**1**), 45% of *p*-chlorophenol (*p*-) and 21% of *o*-chlorophenol (*o*-) (Table 1, run 2). In the presence of H_2O_2 , metal salts showed different activities. Among the tested metal salts, NaCl, CaCl_2 , MgCl_2 , ZnCl_2 , FeSO_4 , FeCl_3 , NiSO_4 , $\text{Co}(\text{OAc})_2$, $\text{Co}(\text{acac})_2$, LiCl, $\text{C}(\text{NO}_3)_2$, $\text{C}(\text{OAc})_2$ and $\text{C}(\text{Br})_2$ had a poor effect (Table 1, runs 3–15), as both the conversions and total yields were lower than those using H_2O_2 alone. Notably, $\text{C}(\text{Cl})_2$ and MnSO_4 indicated high activities; the product distribution showed a dependence on the catalysts. A conversion of 85% for **1** was obtained over $\text{C}(\text{Cl})_2$, the total yield was 83%, containing <1% of **1**, 54% of *p*- and 29% of *o*- (Table 1, run 16). Conversion of **1** over MnSO_4 reached as high as 93% with a total yield of 91%, and the products were 16% of **1**, 49% of *p*-, 26% of *o*- and trace 2,6-dichlorophenol (**1**) (Table 1, run 17). Obviously, MnSO_4 is more effective in the formation of **1**. Meanwhile, various manganese compounds were tested, and the effect of anions on the reactions was tested (Table 1, runs 18–

encapsulated in zeolites with HCl and alkali chlorides/bromides as halogen sources and hydrogen and hydrogen peroxide as oxidants,³² but the selectivity for 2,4-dichloroaromatics was low. Moreover, VOCs (volatile organic compounds) are still present in these systems (Scheme 3).

As for chlorination, we consider a desirable route for the chlorination of phenols with HCl using environmentally friendly oxidants, such as hydrogen or hydrogen peroxide,^{23,32,33} in which chlorine anions are incorporated into the product *via* oxidation and water is the only by-product from the oxidation.

Table 2 Optimization of reaction conditions for the synthesis of 1

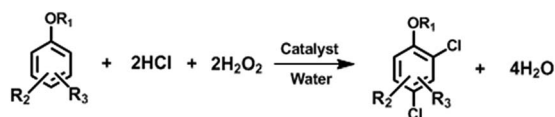
Run	MnSO ₄ (mol%)	T (°C)	HCl : H ₂ O ₂ : 1 (molar ratio)	Conversion ^b (%)	Total yield ^c (%)	Yield ^d (%)			
						1	<i>p</i> -	<i>o</i> -	1
1	1	25	7.1 : 1.9 : 1	93	91	16	49	26	Trace
2	5	25	7.1 : 1.9 : 1	100	82	55	16	9	Trace
3	10	25	7.1 : 1.9 : 1	100	80	57	15	8	Trace
4	1	25	2.4 : 1.9 : 1	76	74	9	39	25	Trace
5 ^e	1	45	2.4 : 1.9 : 1	89	86	25	38	22	1
6 ^e	1	60	2.4 : 1.9 : 1	94	92	41	31	18	Trace
7 ^e	1	80	2.4 : 1.9 : 1	100	95	72	13	9	3
8 ^e	1	90	2.4 : 1.9 : 1	100	83	65	11	5	2
9 ^f	1	80	2.4 : 2.8 : 1	100	97	93	1	Trace	3
10 ^g	1	80	2.1 : 2.8 : 1	100	95	91	1	Trace	3
11 ^g	—	80	2.1 : 2.8 : 1	100	96	34	39	23	Trace
12 ^h	—	80	2.0 : 2.0 : 1	94	91	31	35	25	Trace
13 ^h	1	80	2.0 : 2.0 : 1	85	83	58	15	10	1
14 ^{g,i}	1	80	2.1 : 2.8 : 1	100	93	89	2	Trace	2
15 ^j	1	80	2 : 2.8 : 1	96	92	85	3	2	2
16 ^k	1	80	2.1 : 3.7 : 1	100	88	73	4	2	9

^a Reaction conditions: **1** : 21.3 mmol, HCl: 151.3 mmol, H₂O₂ (30% aq. solution): 4.05 ml, 39.7 mmol, H₂O: 9.8 ml, 3 h. ^b Conversion (%) = [he converted **1** (mol)/initial **1** (mol)] × 100. ^c Total yield (%) = [all products (mol)/initial **1** (mol)] × 100. ^d Yield (%) = [large product (mol)/initial **1** (mol)] × 100. ^e HCl: 50.4 mmol. ^f HCl: 50.4 mmol, H₂O₂ (30% aq. solution): 6.08 ml, 58.8 mmol. ^g HCl: 44.7 mmol, H₂O₂ (30% aq. solution): 6.08 ml, 58.8 mmol. ^h HCl: 42.6 mmol, H₂O₂ (30% aq. solution): 4.35 ml, 42.6 mmol. ⁱ Under Ar atmosphere. ^j HCl: 42.6 mmol, H₂O₂ (30% aq. solution): 6.08 ml, 58.8 mmol. ^k HCl: 44.7 mmol, H₂O₂ (30% aq. solution): 8.10 ml, 79.4 mmol.

Table 3 Optimization of reaction conditions for the synthesis of 1

Run	Time	Conversion ^b (%)	Total yield ^c (%)	Yield ^d (%)			
				1	<i>p</i> -	<i>o</i> -	1
1	100	95	91	1	Trace	3	
3	100	94	90	1	Trace	2	
6	98	92	88	2	Trace	1	

^a Reaction conditions: **1** : 21.3 mmol, MnSO₄: 1 mol%, HCl: 44.7 mmol, H₂O₂ (30% aq. solution): 6.08 ml, 58.8 mmol, H₂O: 9.8 ml, 80 °C, 3 h. ^b Conversion (%) = [he converted **1** (mol)/initial **1** (mol)] × 100. ^c Total yield (%) = [all products (mol)/initial **1** (mol)] × 100. ^d Yield (%) = [large product (mol)/initial **1** (mol)] × 100.



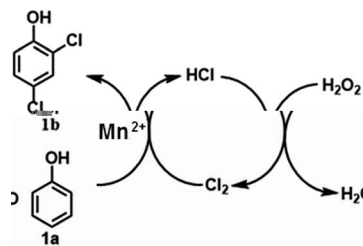
Scheme 5 Chlorination of substituted benzene 1

mol% of MnSO₄ resulted in lower overall yields due to over-oxidation. When the amount of HCl was reduced and HCl : H₂O₂ : 1 was varied to 2.4 : 1.9 : 1, the conversion of **1** was 76% with a total yield of 74%, containing 9% of **1**, 39% of *p*-, 25% of *o*- and trace **1** (Table 2, run 4). A large excess amount of HCl promotes the formation of **1**. The effect of temperature was studied at a HCl : H₂O₂ : 1 ratio of 2.4 : 1.9 : 1 (Table 2, runs 5–8). As the temperature was increased from 45 °C to 90 °C, **1** was completely converted at 80 °C and the total yield was 95%; the yield for **1** reached a maximum of 72% with 13% of *p*-, 9%

of *o*- and 3% of **1**. Further increasing the temperature to 90 °C resulted in over-oxidation and the total yield decreased to 83%. Thus, 80 °C is desirable for the reactions.

When the increased the amount of H₂O₂, i.e. the ratio of HCl : H₂O₂ : 1 was varied from 2.4 : 1.9 : 1 to 2.4 : 2.8 : 1, the yield of **1** reached as high as 93% with 1% of *p*-, trace *o*- and 3% of **1** (Table 2, run 9). If HCl was further decreased and HCl : H₂O₂ : 1 was varied to 2.1 : 2.8 : 1, the total yield was 95%, and the yield for **1** was 91% with 1% of *p*-, trace *o*- and 3% of **1** (Table 2, run 10). In the absence of MnSO₄, the full conversion of **1** with a total yield of 96% was achieved, and the yield for **1** was 34% with 39% of *p*-, 23% of *o*- and trace **1** (Table 2, run 11). When the reaction was carried out based on the theoretical equation (Scheme 4), i.e. HCl : H₂O₂ : 1 was 2.0 : 2.0 : 1, 85% of **1** was converted with a total yield of 83%, and the products were 58% of **1**, 15% of *p*-, 10% of *o*- and 1% of **1** (Table 2, run 13). In the absence of MnSO₄, 94% of **1** was converted with a total yield of 91%, containing 31% of **1**, 35% of *p*-, 25% of *o*- and trace **1** (Table 2, run 12). Obviously, the presence of MnSO₄ significantly increased the yield of **1**, and hence MnSO₄ is key for the selective chlorination of **1** to **1**. When the reaction was performed under an Ar atmosphere (Table 2, run 14), the results were comparable with those in air (Table 2, run 10), so oxygen has no effect on the reactions. If **1** was chlorinated based on a ratio of HCl : 1 : a 2.0 : 1, the yield of **1** was 85% with 3% of *p*-, 2% of *o*- and 2% of **1** (Table 2, run 15). As a large excess amount of H₂O₂ was used (HCl : H₂O₂ : 1 = 2.1 : 3.7 : 1), over-oxidation occurred and the total yield decreased to 88% (Table 2, run 16). Because the decomposition of H₂O₂ is inevitable, the used amount of H₂O₂ in the reaction is higher than the theoretical value. The dilution of H₂O₂ and





Scheme 6

HCl based on the optimized conditions (Table 2, run 10) is 66% and 87%, respectively.

When HCl : H₂O₂ : 1 as 3.1 : 4.2 : 1, full conversion of 1 was achieved at 80 °C for 3 h and the total yield was 91%, the yield for 2,4,6-trichlorophenol was 73% with 11% of 1, 7% of 1 and trace *p*- and *o*-. If HCl : H₂O₂ : 1 was increased to 3.5 : 4.2 : 1, full conversion of 1 with a total yield of 94% was obtained, and 80% of 2,4,6-trichlorophenol with 6% of 1 and 8% of 1 were found as the products. Thus, while the performance of MnSO₄ is better in the synthesis of 1, it is also active in the synthesis of 2,4,6-trichlorophenol.

In our experiments, we found that the reagents formed a homogeneous solution before reaction, and no discrete phases were observed at the end of the reaction. The top phase is an aqueous solution containing the catalysts, and the lower is an organic phase mainly composed of 1, *p*-, *o*- and 1. This means that the products automatically come from the aqueous solution. This property is really convenient for product collection via phase separation. Moreover, since MnSO₄ remains in the aqueous solution, recycling of the catalysts is simple.

In fact, commercial hydrochloric acid can be directly used rather than gaseous HCl in the reactions, as similar results were also obtained under the optimized conditions. However, we think that the use of gaseous HCl is more economical, particularly for large scale production. If hydrochloric acid is used, the products can be obtained by phase separation, but the collection of the catalysts requires the removal of the whole aqueous solution via evaporation. Then, the collected catalysts, 1 and hydrochloric acid are mixed for the next run. As gaseous HCl is used, the products are isolated by phase separation, the remaining aqueous solution is concentrated by removing excess water from the solution of H₂O₂ under reduced pressure, and gaseous HCl is introduced into the concentrated solution. Then, 1 is added for the next run. Compared with gaseous HCl, it is clear that more water needs to be evaporated when using hydrochloric acid.

Based on the optimized conditions, the recycling results of the catalysts are shown in Table 3. After each run, the same procedure was performed in the catalysts as used 6 times. These results indicate that the catalysts are recyclable, and no significant decrease in activity was observed even after 6 runs.

Since 2,4-dichloro-substituted phenol derivatives present a series of valuable materials for fine chemicals, this method

as further studied in the chlorination of various phenol derivatives (see ESI, Table S1†). Although monochloro-substituted phenols, such as *p*- and *o*-, are undesirable products in our reactions, these compounds can be efficiently converted into 1 in our method. Complete conversion of *p*- was obtained in a high yield of 96% for 1, and the yield of 1 was 94% for the total conversion of *o*-. Thus, monochloro-substituted phenols can be efficiently utilized, and the by-product always remains in our system only 1. As for bromo- or iodo-substituted phenols, side-reactions of debromination/deiodination occurred and resulted in a complex mixture. This method is effective for alkylphenols, which were successfully chlorinated as various 2,4-dichlorophenols. A yield of 75% was achieved for 3 from *o*-cresol (3), and an 81% yield for 4 was obtained from 2-*tert*-butylphenol (4). Complete conversion of 5 (3,5-dimethylphenol) was achieved, and the yield for 5 was 86%. The chlorination of ethers of phenol can also be easily performed under similar conditions. Complete conversion of anisole () led to a yield of 82% for , and a high yield of 81% for was achieved from 3,5-dimethyl anisole (). Thus, we consider that our method offers a versatile synthetic method in the manufacture of various 2,4-dichlorophenol derivatives (Scheme 5).

The molar ratio of H₂O₂ : 1 as 2 : 1 according to the theoretical equation (Scheme 4), but as 2.8 : 1 under the optimized conditions (Table 2, run 10). The used amount of H₂O₂ is higher than the theoretical value. It is well known that the catalytic decomposition of H₂O₂ over metal ions is inevitable, and the interactions of Mn²⁺ with H₂O₂ lead to non-productive species, such as oxygen atoms, active oxygen species or OH[•]/OOH[•] radicals, which are possible active species for reactions. In our experiments, when a free radical scavenger, 2,6-di-*tert*-butyl-4-methylphenol, was added in our reactions, the yield of 1 significantly decreased to 30%. Although this result indicates that a free radical pathway is possible in our reactions, our attempts to find out the free radicals or active species failed because of the complexity of this system. In controlled experiments, we found that the addition of H₂O₂ into an aqueous solution of HCl immediately resulted in light yellow gas, which was Cl₂ based on GC-MS analysis. Thus, while the free radicals or active species are not clear, the main pathway can be presented as shown in Scheme 6: HCl is oxidized by H₂O₂ to Cl₂; the generated Cl₂ reacts with 1 to form 1 with the release of HCl, which is re-oxidized and recycled in 1 is established. Details of the reaction mechanism are under investigation, and we will report the results in future.

Conclusions

In summary, we have developed a simple, mild and efficient method for the chlorination of phenol to 2,4-dichlorophenol catalyzed by manganese(II) sulfate in the liquid phase. In this system, hydrogen chloride was used as a chlorinating agent, hydrogen peroxide as an oxidant and water as a solvent. We envisage that our method will be effective in the manufacture of various 2,4-dichlorophenol derivatives based on the following



reasons: (1) high activity and selectivity; (2) VOC free; (3) simple production and recyclable catalysts.

Experimental section

Phenol and catalyst were added together in a three-neck flask equipped with a gas inlet, a liquid inlet and a reflux condenser (open to air). Gaseous HCl was introduced and dissolved as an aqueous solution. The flask was immersed in a preheated oil bath and vigorously stirred with a magnetic stirrer. Then, H₂O₂ (30% aq. solution) was added dropwise by a channel pump during the reaction. At the end of the reaction, the mixture was left to stand for 1.5 h, and an isolated organic phase from the aqueous solution formed a white foam. The organic phase was collected and diluted with acetone to prepare the sample for quantitative analysis. The conversions and yields were determined by gas chromatography. Each experiment was reproduced at least three times. The experimental error in the determination of the conversions and yields normally did not exceed 4%. Products were obtained by column chromatography using silica gel (pore diameter) and confirmed by GC-MS, ¹H and ¹³C NMR.

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2,4- **-3,5-** **1**. ¹H NMR (600 MHz, CDCl₃) δ: 7.32 (d, *J* = 2.4 Hz, 1H), 7.15 (dd, *J* = 2.4, 9.6 Hz, 1H), 6.95 (d, *J* = 9.0 Hz, 1H), 5.51 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ: 150.2, 128.6, 128.56, 125.6, 120.4, 117.1.

4- **1**. ¹H NMR (600 MHz, CDCl₃) δ: 7.19 (d, *J* = 9.0 Hz, 2H), 6.76 (d, *J* = 8.4 Hz, 2H), 4.90 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ: 154.1, 129.6, 125.7, 116.7.

2- **1**. ¹H NMR (600 MHz, CDCl₃) δ: 7.29 (m, 1H), 7.16 (m, 1H), 7.01 (m, 1H), 6.85 (m, 1H), 5.62 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ: 151.4, 129.1, 128.5, 121.4, 119.9, 116.3.

2, **-** **1**. ¹H NMR (600 MHz, CDCl₃) δ: 7.26 (d, *J* = 7.8 Hz, 2H), 6.82 (t, *J* = 8.4 Hz, 1H), 5.85 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ: 147.9, 128.3, 121.2, 121.1.

2,4, **-** **1**. ¹H NMR (600 MHz, CDCl₃) δ: 7.28 (s, 2H), 5.81 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ: 146.9, 128.1, 125.4, 121.6.

2,4- **-** **1**. ¹H-NMR (600 MHz, CDCl₃) δ: 7.16 (d, *J* = 2.4 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 5.24 (s, 1H), 2.26 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ: 148.4, 129.6, 127.3, 125.8, 124.7, 119.8, 16.3.

2,4- **-** **-** **1**. ¹H-NMR (600 MHz, CDCl₃) δ: 7.20 (d, *J* = 2.4 Hz, 1H), 7.15 (d, *J* = 2.4 Hz, 1H), 5.80 (s, 1H), 1.38 (s, 9H); ¹³C NMR (150 MHz, CDCl₃) δ: 148.5, 138.9, 126.2, 125.9, 124.7, 121.1, 35.5, 29.1.

2,4- **-3,5-** **1**. ¹H-NMR (600 MHz, CDCl₃) δ: 6.80 (s, 1H), 5.48 (s, 1H), 2.46 (s, 3H), 2.32 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ: 149.5, 136.0, 134.2, 126.5, 118.5, 115.1, 20.8, 18.3.

2,4- **1**. ¹H NMR (600 MHz, CDCl₃) δ: 7.34 (d, *J* = 2.4 Hz, 1H), 7.19 (dd, *J* = 2.4, 9.0 Hz, 1H), 6.82 (d, *J* = 9.0 Hz,

1H), 3.86 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ: 153.9, 129.9, 127.9, 125.6, 123.2, 112.8, 56.3.

2,4- **-3,5-** **1**. ¹H NMR (600 MHz, CDCl₃) δ: 6.67 (s, 1H), 3.86 (s, 3H), 2.47 (s, 3H), 2.36 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ: 153.2, 136.3, 134.9, 126.8, 120.9, 111.4, 59.3, 21.2, 18.2.

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