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Iron Catalysis for Room-Temperature Aerobic Oxidation of Alcohols to Carboxylic Acids

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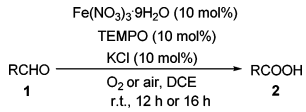
Supporting Information

ABSTRACT: Oxidation from alcohols to carboxylic acids, a class of essential chemicals in daily life, academic laboratories, and industry, is a fundamental reaction, usually using at least a stoichiometric amount of an expensive and toxic oxidant. Here, an efficient and practical sustainable oxidation technology of alcohols to carboxylic acids using pure O_2 or even O_2 in air as the oxidant has been developed: utilizing a catalytic amount each of $Fe(NO_3)_3·9H_2O$/TEMPO/MCl, a series of carboxylic acids were obtained from alcohols (also aldehydes) in high yields at room temperature. A 55 g-scale reaction was demonstrated using air. As a synthetic application, the first total synthesis of a naturally occurring allene, i.e., phlomic acid, was accomplished.

As one of the most abundant metals in earth's crust, iron is widely distributed in nature. Of particular interest, the heme iron compounds in hemoglobin play an important role in molecular oxygen transportation and activation in life at ambient temperature.[1] Iron is also a part of oxidative enzymes.[2] Thus, iron catalysts[3] may be a potentially viable catalyst for aerobic oxidation of alcohols to acids. On the other hand, the oxidation from alcohols to carboxylic acids is one of the most fundamental chemical transformations with great potential for daily life, academic research, and industry.[4] Traditionally, toxic and expensive oxidants such as $KMnO_4$,[5] CrO_3,[6] etc. have to be used, which would cause severe environmental burden due to the formation of waste from at least stiochiometeric amounts of these oxidants, thus, it is highly desirable to develop environmentally friendly new oxidization protocols. Molecular oxygen is a clean, atom economic, and sustainable oxidant. Although aerobic oxidation of alcohols to aldehydes is becoming a mature technology,[7] the process toward carboxylic acids remains to be a fundamental challenge since few studies on aerobic oxidization of alcohols to carboxylic acids have been reported with rather limited success or scope even with noble metal catalyst(s).[8−16] Here, we wish to report an efficient protocol with a broad scope and selectivity using a readily available iron catalyst and TEMPO under pure oxygen or air conditions.

Based on the above literature data, the challenge to obtain carboxylic acids from alcohols via aerobic oxidation may be in the process of transforming aldehydes to carboxylic acids since most such aerobic oxidations of alcohols stop at the stage of aldehydes.[7,17−19] During further study of selective oxidation of alcohols to aldehydes catalyzed by $Fe(NO_3)_3·9H_2O$ and TEMPO,[19] we observed that when lauraldehyde **1a** was treated with 10 mol % each of $Fe(NO_3)_3·9H_2O$, TEMPO, and KCl with an O_2 balloon in DCE at rt for 12 h, 94% isolated yield of lauric acid **2a** was formed. This recipe could be applied to the oxidation of normal alkyl aliphatic aldehydes (Table 1, entries 1 and 3), cyclohexane-carboxaldehyde **1b** (Table 1, entry 2), 3-phenyl-propanal **1d** (Table 1, entry 4) to the corresponding carboxylic acids **2a**−**2d** in high yields. In addition, the yield remains high when a balloon of air was applied instead of pure O_2.

Table 1. Aerobic Oxidation of Aldehydes Using O_2 or Air as Oxidant[a]

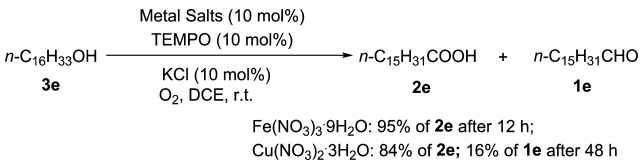


entry	substrate	product	yield of **2** (%)[b] O_2	Air
1	n-$C_{11}H_{23}CHO$ (**1a**)	n-$C_{11}H_{23}CO_2H$ (**2a**)	94	88
2	CyCHO (**1b**)	$CyCO_2H$ (**2b**)	90	83
3	n-$C_7H_{15}CHO$ (**1c**)	n-$C_7H_{15}CO_2H$ (**2c**)	96	97
4	$Ph(CH_2)_2CHO$ (**1d**)	$Ph(CH_2)_2CO_2H$ (**2d**)	96	98

[a]The reaction was carried out on a 1.0 mmol scale of **1** in 4.0 mL of DCE with a bag of O_2 or air. [b]Isolated yield.

With these observations, we attempted to apply this recipe to the direct oxidation of alcohols into carboxylic acids: Cetyl alcohol **3e** was oxidized to palmitic acid **2e** within 12 h under standard conditions (Scheme 1). We screened different nitrates and observed that $Co(NO_3)_3·6H_2O$ (**3e** recovery 84%), $Ni(NO_3)_3·6H_2O$ (**3e** recovery 83%) and $Zn(NO_3)_2·6H_2O$ (**3e** recovery

Scheme 1. Aerobic Oxidation of 3e with Different Metal Nitrates



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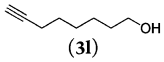
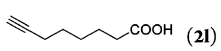
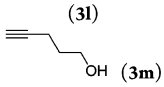
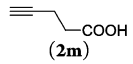
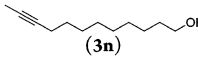
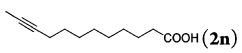
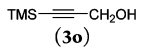
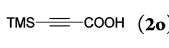
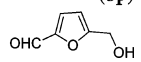
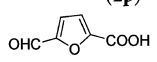
100%) were not effective at all. $Cu(NO_3)_2{\cdot}3H_2O$ worked much slower (Scheme 1).

With standard conditions in hand, we explored the generality of the reaction with various alcohols. Apart from aliphatic alcohols (Table 2, entries 1, 2, and 4) and 3-phenylpropanol (Table 2, entry 3), the aerobic oxidation also tolerates synthetically useful functional groups: ester (Table 2, entries 5−6), heterocycle (Table 2, entries 7−8), halogen (Table 2, entry 9), and ether (Table 2, entry 10) have all been well tolerated. Alcohols with a terminal or nonterminal C−C triple bond could all be oxidized to acids in moderate or high yields (Table 2, entries 11−13). TMS-substituted propargyl alcohol could be converted into the corresponding acid under both O_2 and air conditions when extending the time to 36 and 48 h (Table 2, entry 14). 3-Cyclohexene-1-methanol (**3p**) could be oxidized to **2p** smoothly with 20 mol % of TEMPO (Table 2, entry 15). Two examples of arylmethyl alcohols are also presented (Table 2, entries 16 and 17).

Table 2. Aerobic Oxidation of Alcohols Using O_2 or Air as Oxidant[a]

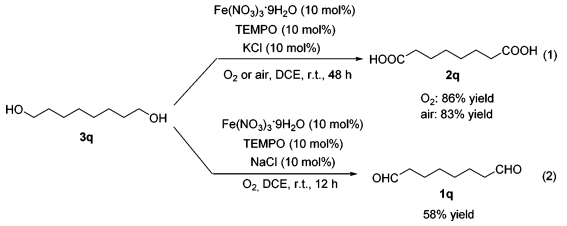
Entry	Alcohol	Product	Yield of **2** (%)[b] O_2	Yield of **2** (%)[b] Air
1	*n*-$C_{12}H_{25}OH$ (**3a**)	*n*-$C_{11}H_{23}CO_2H$ (**2a**)	100	95
2	*n*-$C_8H_{17}OH$ (**3c**)	*n*-$C_7H_{15}CO_2H$ (**2c**)	85	89
3	$Ph(CH_2)_3OH$ (**3d**)	$Ph(CH_2)_2CO_2H$ (**2d**)	98	99
4	*n*-$C_{16}H_{33}OH$ (**3e**)	*n*-$C_{15}H_{31}CO_2H$ (**2e**)	99	98
5	$MeO_2C(CH_2)_5OH$ (**3f**)	$MeO_2C(CH_2)_4CO_2H$(**2f**)	94	86
6	$AcO(CH_2)_8OH$ (**3g**)	$AcO(CH_2)_7CO_2H$ (**2g**)	93	93
7	 (**3h**)	 (**2h**)	70	73
8	 (**3i**)	 (**2i**)	85	81
9	$Br(CH_2)_9OH$ (**3j**)	$Br(CH_2)_8CO_2H$ (**2j**)	98	98
10	*n*-$C_6H_{13}O(CH_2)_2OH$ (**3k**)	*n*-$C_6H_{13}OCH_2CO_2H$ (**2k**)	92	84
11	 (**3l**)	 (**2l**)	80	80
12	 (**3m**)	 (**2m**)	60	68
13	 (**3n**)	 (**2n**)	95	90
14	 (**3o**)	 (**2o**)	66[c]	65[d]
15	 (**3p**)	 (**2p**)	81[d,e]	70[d,e]
16			55[d,e,f]	-
17	*p*-nitrobenzyl alcohol	4-nitrobenzoic acid	76[d]	-

[a]Reaction was carried out on a 1.0 mmol scale of **3** in 4.0 mL of DCE with a bag of O_2 (12 h) or air (16 h). [b]Isolated yield. [c]Reaction time was 36 h. [d]Reaction time was 48 h. [e]20 mol % TEMPO was used. [f]20 mol % of $Fe(NO_3)_3{\cdot}9H_2O$ was used.

We could prepare octanedioic acid under the standard O_2 or air conditions using 10 mol % KCl within 48 h (Scheme 2, eq 1) or 1,8-octane-dial using 10 mol % NaCl within 12 h, from 1,8-octanediol, respectively, with a high selectivity (Scheme 2, eq 2, and the data in SI).[19]

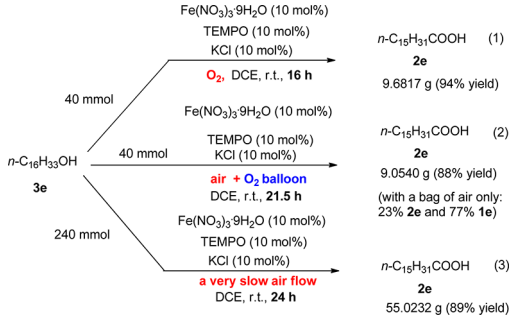
To further demonstrate the practicality of the catalytic system, a 40 mmol reaction of cetyl alcohol **3e** was conducted using pure O_2 to give 9.6817g of palmitic acid **2e** in 94% isolated yield (Scheme 3, eq 1 and apparatus (a) in SI). The purification of product only requires simple recrystallization of the crude product after

Scheme 2. Selective Oxidation of 1,8-Octanediol



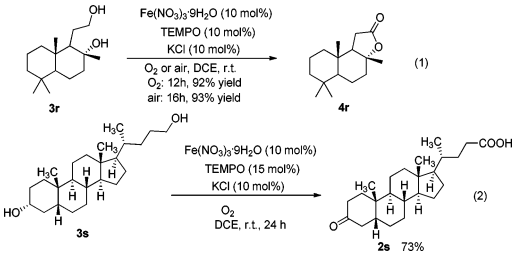
removing the solvent instead of column chromatography. The reaction on the same scale may also be conducted by using a bag of air (size: 70 L, oxygen bag used in hospital) for 1.5 h first, which was followed by the supplement of a bag of pure O_2 (commercial size: 2 L, may be expanded to 5 L, the white gas bag in apparatus (b) in SI) to provide the consumed oxygen in the air bag efficiently (Scheme 3, eq 2 and apparatus (b) in SI). Such a practice avoids the unsafe high concentration of pure O_2 over DCE to make the procedure safer. The same reaction using a bag of air only was incomplete affording acid **2e** (23% yield by NMR) and aldehyde **1e** (77% yield by NMR). Furthermore, by applying a slow flow of air, the reaction was also easily conducted on the scale of 240 mmol scale in 89% isolated yield (Scheme 3, eq 3 and apparatus (c) in SI).[20]

Scheme 3. Large-Scale Reactions with O_2 or Air



The sesquiterpenediol **3r** could also be oxidized to sclareolide **4r** in high yield with both pure O_2 or air (Scheme 4, eq 1).

Scheme 4. Aerobic Oxidation of Alcohols 3r and 3s



Substrate **3s** bearing a steroid skeleton could also be oxidized to the corresponding acid **2s** smoothly in 73% yield with the secondary alcohol in the molecule **3s** being oxidized to the ketone group as well (Scheme 4, eq 2).

Furthermore, the reaction was applied to the first total synthesis of phlomic acid, a naturally occurring axially chiral allene, which was isolated from *Phlomis* in 1997.[21] By applying enantioselective allenation of alkynes reaction (EATA)[22] developed in our group as the key step for the formation of the chiral allene entity, we reasoned that phlomic acid (R_a)-**5a** could be synthesized from

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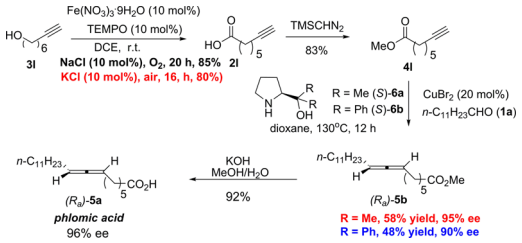
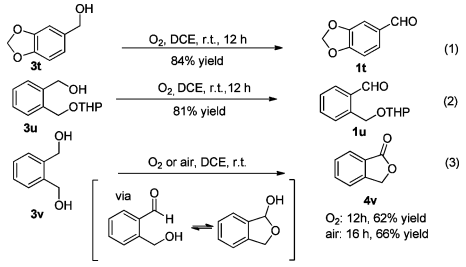
terminal alkyne **3l** and aldehyde **1a** (Scheme 5). Thus, 7-octynoic acid was prepared from 7-octyn-1-ol in 80% yield using 10 mol % each of $Fe(NO_3)_3{\cdot}9H_2O$/TEMPO/KCl catalyst in air. After esterification, ester **4l** was submitted to the EATA reaction. After screening of different prolinol derivatives, we found that when (*S*)-dimethylprolinol was used for the first time in the $CuBr_2$-catalyzed EATA reaction, product (R_a)-**5b** with 95% ee could be prepared in 58% yield, while with (*S*)-diphenylprolinol, the ee dropped to 90%. (R_a)-**5b** was treated with KOH in MeOH/H_2O at 60 °C to yield phlomic acid ((R_a)-**5a**) in 92% yield and 96% ee.

Scheme 5. Total Synthesis of Phlomic Acid Using Aerobic Oxidation and EATA



In addition, it was observed that the oxidation of benzylic alcohol such as piperitol (**3t**) or mono THP-protected 1,2-benzenedimethanol (**3u**) stopped mostly at the stage of aldehyde (Scheme 6, eqs 1−2). However, reaction of 1,2-benzenedimethanol (**3v**) gave 62% yield of isobenzofuran-1(3*H*)-one (**4v**) (Scheme 6, eq 3), indicating the possibility of the oxidation to aldehyde, then forming the corresponding hemiacetal, which was further oxidized to lactone.

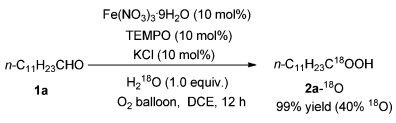
Scheme 6. Aerobic Oxidation of Benzylic Alcohol and 1,2-Benzenedimethanol[a]



[a]Conditions: $Fe(NO_3)_3{\cdot}9H_2O$ (10 mol %), TEMPO (10 mol %), KCl (10 mol %)

When the oxidation reaction of lauraldehyde **1a** was conducted in the presence of 1 equiv of $H_2{}^{18}O$, lauric acid **2a**-^{18}O was isolated in 99% yield with 40% ^{18}O incorporation, indicating the involvement of H_2O in the reaction process. The lower level of ^{18}O incorporation was caused by the 0.9 equiv of H_2O in 10 mol % of $Fe(NO_3)_3{\cdot}9H_2O$ and the in situ generated water (see Scheme 7 and Scheme 9).

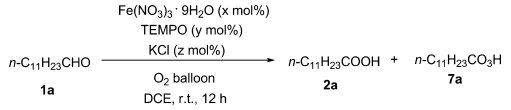
Scheme 7. Isotopic ^{18}O Distribution Experiment with 1a



As a further evidence, reddish brown gas (NO_2) was observed during the reaction, and NO was detected by GS-MS (see SI for experimental details). We also observed that alcohol **3a** was completely consumed within 6 h, generating aldehyde **1a** as the initial product. Acid **2a** emerged after 2 h (pages S36−S37, SI). As a comparison, the same reaction with 10 mol % of NaCl failed to afford the formation of the carboxylic acid **2a** within 4 h (pages S38−S39, SI). Furthermore, the reaction with 5 mol % each of $Fe(NO_3)_3{\cdot}9H_2O$, TEMPO, and NaCl, the reaction conditions in the previous report,[19] led to the highly selective formation of aldehyde-No acid was formed (pages S40−S41, SI). The counterion effect of inorganic chloride on the oxidation is as follows: $K^+ \sim Rb^+ > Cs^+ \sim Na^+ > Mg^{2+} \sim Zn^{2+} > Bu_4N^+$ (pages S36−S51, SI), which is in accordance of the basicity order (although not a linear one);[23] when 18-crown-6 or kryptofix 222 (a typical cryptand) was used together with KCl, the reaction became much slower, indicating an obvious effect of the cation (pages S52−S55, SI).

In addition, control experiments showed that the oxidation of aldehyde **1a** in oxygen alone failed to afford the acid **2a** (Table 3, entry 2); the reaction in the absence of KCl is slower (Table 3, entry 3); as reported,[24] Fe(III) alone may afford peroxy acid **7a**, via the reaction of the acyl radical intermediate with oxygen. This peroxy acid may react with the starting aldehyde to afford the acid **2a** finally as a mixture (Table 3, entry 4); in the absence of TEMPO, the reaction is slower, and the formation of peroxy acid was also observed (Table 3, entry 5); as a comparison under the standard reaction condition, the formation of peroxy acid **7a** was not detected (Table 3, entry 1). The reaction could not occur without $Fe(NO_3)_3{\cdot}9H_2O$ (Table 3, entry 6).

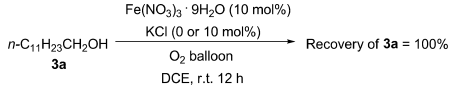
Table 3. Aerobic Oxidation of Aldehyde 1a: The Role of Each Catalytic Component



entry	$Fe(NO_3)_3{\cdot}9H_2O$ (x mol %)	TEMPO (y mol %)	KCl (z mol %)	NMR yield, % 1a	2a	7a
1	10	10	10	0	95	0
2	–	–	–	98	2	0
3	10	10	–	14	81	0
4	10	–	–	0	78	11
5	10	–	10	15	64	12
6	–	10	10	100	0	0

However, no reaction was observed for alcohol **3a** in the absence of TEMPO (Scheme 8).

Scheme 8. Aerobic Oxidation of 3a



Based on these observations, we proposed a rationale for this aerobic oxidation (Scheme 9). **Int 1**, the coupling product of TEMPO and Fe^{3+},[25] reacted with the alcohol to form **Int 2**. **Int 2** produced the aldehyde, TEMPOH, and Fe^{2+} after β-H elimination and reductive elimination. Fe^{2+} would be reoxidized to Fe^{3+} by NO_2 in the reaction system, while NO_2[26] was reduced to NO and

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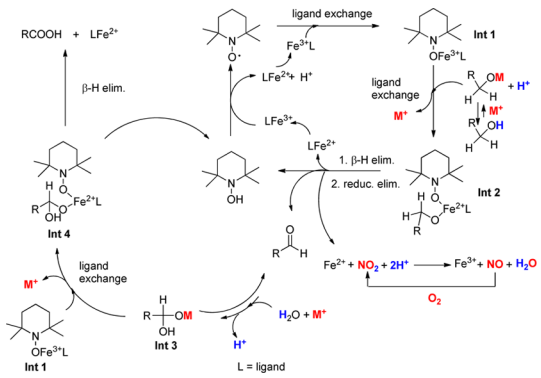
regenerated by its reaction with O_2. TEMPOH was converted back into TEMPO by its reaction with Fe^{3+}. The metalated aldehyde hydrate **Int 3** was formed by attack of H_2O at the aldehyde mediated by Fe^{3+}. **Int 3** would undergo a similar process to produce the carboxylic acid. As noted in our previous report, the reaction in the absence of NaCl is slow, and the chloride may be working as the ligand (L) to iron.[19] According to data with different MCl in SI, different M^+ may have a different effect on the ligand exchange rate for the formation of **Int 2**–**4**. However, further studies are required for the mechanism.

Scheme 9. A Proposed Mechanism: The Possible Role of the Cation



In summary, we developed a practical and efficient environmentally benign catalytic protocol of $Fe(NO_3)_3{\cdot}9H_2O$/TEMPO/MCl to accomplish the oxidation of alcohols to carboxylic acids using O_2 or air as terminal oxidant at room temperature. The reaction may be easily conducted on a 9–55 g-scale with pure O_2, air/pure O_2 or air flow conditions. First total synthesis of natural product phlomic acid was accomplished using this aerobic oxidation protocol and EATA. Further studies especially the mechanism are being actively pursued in this laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b03948.

Experimental details and data (PDF)

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Notes

The authors declare no competing financial interest.

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(20) Caution: Oxygen in use in combination with organic solvents; remove all ignition sources including sources of sparks, static, or flames since oxygen increases intensity of any fire. Inhalation of pure oxygen should be avoided as well. The flash point of DCE is 13 °C. Lower and upper explosive limit of DCE in air is 6.2% and 16.0%. For more information, see: Cheremisinoff, N. P. *Handbook of Hazardous Chemical Properties*; Butterworth-Heinemann: Woburn, MA, 1999. Yaws, C. L. *Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds*; Knovel: New York, 2003.

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