JOC Note

Selective Aerobic Oxidation of Activated Alcohols into Acids or Aldehydes in Ionic Liquids

Nan Jiang and Arthur J. Ragauskas*

School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

arthur.ragauskas@chemistry.gatech.edu

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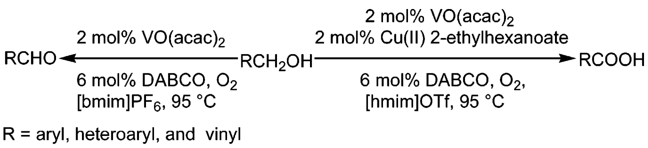

Selective aerobic oxidation of activated primary alcohols into acids or aldehydes has been developed in ionic liquids. Under optimal conditions, various alcohols could be selectively converted into their corresponding acids or aldehydes in good to excellent yields. The newly developed catalytic systems could also be recycled and reused for three runs without any significant loss of catalytic activity.

Alcohol oxidation is an important transformation from the viewpoint of organic synthesis and industrial manufacturing.[1] Many oxidations of this type are carried out using stoichiometric amounts of oxidizing reagents (i.e., $KMnO_4$, MnO_2, CrO_3, Br_2, etc.)[2] with considerable drawbacks such as high cost, waste byproducts, and serious environmental issues. In comparison, molecular oxygen may serve as superior oxidant that is of lower cost, greater abundance, and improved safety. Furthermore, the use of molecular oxygen as the primary oxidant may also have the advantage that water is the sole final byproduct. Thus, catalytic aerobic alcohol oxidation represents a promising protocol for organic synthesis and industrial applications. Accordingly, there has been concerted effort directed at developing various transition metals (mainly copper,[3] palladium,[4] ruthenium,[5] and vanadium[6]) to catalyze aerobic alcohol oxidation.

On the other hand, ionic liquids, composed entirely of ions with a melting point below 100 °C,[7] have attracted increasing interest in the effort of reduction or replacement of volatile organic compounds (VOCs) from the reaction media in the area of Green Chemistry focus.[8] Although ionic liquids have been recognized as alternative green chemistry reaction media because of their unique properties, including low volatility, high polarity, good stability over a wide temperature range, and selective dissolving capacity by a proper choice of cation and anion, the use of ionic liquids to immobilize and recycle homogeneous catalysts has become one of the most fruitful areas of ionic liquids research to date.[9] In particular, the advantages of ionic liquids as reaction media for transition-metal-catalyzed oxidation have recently been recognized.[10]

Recently, we reported an efficient vanadium-catalyzed selective aerobic oxidation of alcohols into aldehydes and ketones in the ionic liquid, $[bmim]PF_6$.[11] In light of our recent success in the oxidation of primary alcohols into aldehydes, we turned

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* To whom correspondence should be addressed.

(1) (a) Hudlick, M. *Oxidations in Organic Chemistry*; American Chemical Society: Washington, DC, 1990. (b) Larock, R. C. *Comprehensive Organic Transformations*; Wiley: New York, 1999.

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SCHEME 1. Vanadium-Catalyzed Aerobic Alcohol Oxidation

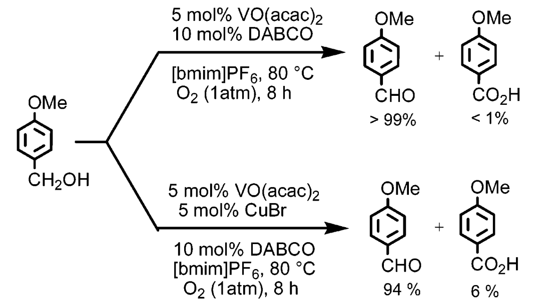
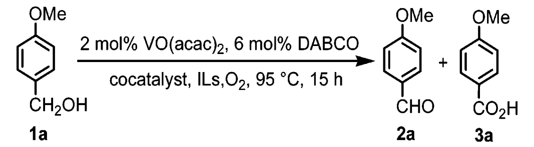


TABLE 1. Optimization of Aerobic Oxidation of 4-Methoxybenzyl Alcohol[a,b]



entry	cocatalyst 2 mol %	ILs	ratio[c] **1a**:**2a**:**3a**	yield (%)[d] **2a**	**3a**
1	none	[bmim]PF_6	0:99:1	90	
2	CuBr	[bmim]PF_6	0:90:10		
3	CuCl	[bmim]PF_6	0:97:3		
4	$CuBr_2$	[bmim]PF_6	0:91:9		
5	$Cu(OAc)_2$	[bmim]PF_6	0:85:5		
6	$Cu(acac)_2$	[bmim]PF_6	0:95:5		
7	Cu(II) 2-ethylhexanoate	[bmim]PF_6	0:74:26	65	16
8	Cu(II) 2-ethylhexanoate	[bmpy]PF_6	0:89:11		
9	Cu(II) 2-ethylhexanoate	[bmpyr]NTf_2	0:66:34		
10	Cu(II) 2-ethylhexanoate	[hmim]OTf	0:13:87		77
11[e]	Cu(II) 2-ethylhexanoate	[hmim]OTf	94:6:0		
12[f]	none	[hmim]OTf	0:92:8		

[a] Reaction conditions: 2 mmol 4-methoxybenzyl alcohol, 2 mol % $VO(acac)_2$, 2 mol % cocatalyst, 6 mol % DABCO, 1 atm O_2, 0.30 g of ionic liquid, 95 °C for 15 h. [b] No ester was detected by ^1H NMR analysis of the crude product mixture in all the cases. [c] The ratio is determined by ^1H NMR analysis of the crude reaction mixture. [d] Isolated yield by flash chromatography. [e] No $VO(acac)_2$ was added. [f] The reaction was run for 48 h.

our attention to the more challenging oxidation of activated primary alcohols into acids.[12] Herein, we wish to report the selective aerobic oxidation of activated primary alcohols into acids or aldehydes with ionic liquids as the solvents.

While developing vanadium-catalyzed aerobic alcohol oxidation, we found that copper salt, CuBr, as the cocatalyst could lead to the overoxidized product 4-methoxybenzoic acid (see Scheme 1). To explore the scope of this reaction, we examined various copper complexes as the cocatalyst for this catalysis in various ionic liquids.

In our initial optimization experiments, 4-methoxybenzyl alcohol was used as the substrate in the presence of 2 mol % $VO(acac)_2$ and 6 mol % DABCO (1,4-diazabicyclo[2.2.2]octane) at 95 °C for 15 h, and the results are summarized in Table 1. After screening various copper complexes in [bmim]PF_6, copper(II) 2-ethylhexanoate was determined to be the most effective cocatalyst to yield 4-methoxybenzoic acid (Table 1, entry 7). Considering the significant effect of ionic liquids on the reaction rate in our previous study,[11] selected imidazolium-type ionic liquid [hmim]OTf (1-hexyl-3-methylimidazolium trifluoromethansulfonate), pyridinium-type ionic liquid [bmpy]-PF_6 (1-butyl-4-methylpyridinium hexafluorophosphate), and pyrrolidinium-type ionic liquid [bmpyr]NTf_2 (1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide) were also tested to improve this transformation (Table 1, entries 8−10). Ionic liquid [hmim]OTf proved to be the optimal, and 4-methoxybenzoic acid was detected as the major product with 77% isolated yield (Table 1, entry 10). It has to be noted that both vanadyl acetylacetonate and copper (II) 2-ethylhexanoate as catalysts are crucial for this oxidation of 4-methoxybenzyl alcohol into 4-methoxybenzoic acid, and very low conversion of 4-methoxybenzyl alcohol into acid (8% conversion after 48 h) in the absence of copper (II) 2-ethylhexanoate or no acid in the absence of vanadyl acetylacetonate was detected by ^1H NMR analysis of the crude reaction mixtures (Table 1, entries 11 and 12).[13] Moreover, no ester (4-methoxybenzyl 4-methoxybenzoate) was detected by ^1H NMR analysis in all the cases.

Subsequently, the catalytic systems were then applied to various primary alcohols as summarized in Table 2. It is clear that all the benzylic alcohols could be selectively oxidized into aldehydes or acids in good to excellent isolated yields and electronic variation on the aromatic substients did not diminish the efficiency and selectivity (Table 2, entries 1−5). *trans*-Cinnamyl alcohol was also selectively converted into the corresponding aldehyde or acid with stereochemical retention of the double bond (Table 2, entry 6). It has to be noted that heteroatom-containing (N, S) substrates (2-pyridine methanol and 2-thiophene methanol) turned out to be compatible with the employed reaction conditions, and the corresponding aldehydes or acids were obtained in good yields (Table 2, entries 7 and 8). Similar to our previous study,[11] the aliphatic alcohol, 3-phenyl-1-propanol, is unreactive to the present catalytic systems, and longer reaction time and elevated temperature failed to afford the corresponding aldehyde or acid (Table 2, entry 9). 4-Methylbenzaldehyde can also be smoothly oxidized into 4-methylbenzoic acid in the presence of $VO(acac)_2$ and copper (II) 2-ethylhexanoate in 12 h, but the absence of $VO(acac)_2$ led to very low conversion of aldehyde into acid (Table 2, entry 10).[14] Due to our special interest in oxidation of lignin-like structures,[15] we next examined the aerobic oxidation of two lignin model compounds,[16] 3,4-dimethoxybenzyl alcohol and 1-(3,4-dimethoxyphenyl)ethanol. Although, 3,4-dimethoxyben-

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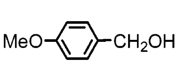
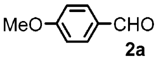
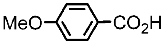
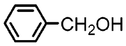
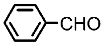
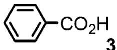
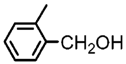
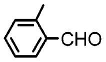
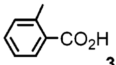
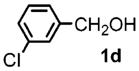
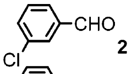
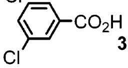
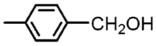
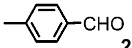
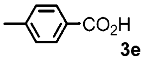
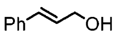
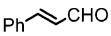
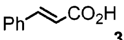
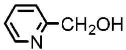
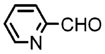
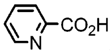
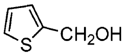
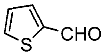
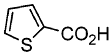
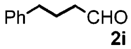
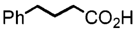
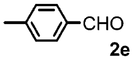
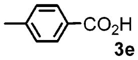
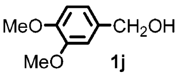
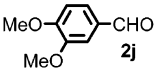
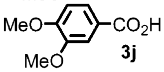
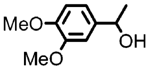
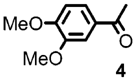
[12] The benzylic or allylic alcohol was oxidized into the aldehyde in high selectivity due to conjugation of the carbonyl group deactivating the further oxidation of the intermediate aldehyde, see : van Bekkum, H.; Lichtenthaler, F. W. *Carbohydrates as Organic Raw Meterials*; VCH: Weinheim, 1990; p. 289.

[13] It is noteworthy that the same oxidation proceeded much slower (11% conversion of alcohol into acid after 12 h) when 2 mol % $VO(acac)_2$ and 2 mol % $Ni(acac)_2$ were employed as the catalysts, despite the fact that $Ni(acac)_2$ has been reported to catalyze the aerobic oxidation of various aromatic aldehydes into acids in the ionic liquid [bmim]PF_6, see: Howarth, J. *Tetrahedron Lett.* **2000**, *41*, 6627.

[14] In the present catalytic system, copper (II) 2-ethylhexanoate could work as the oxygen-activating cocatalyst, and the vanadium could be the active catalyst for the further oxidation of aldehydes into acids, which could be partly confirmed by the fact that copper (II) 2-ethylhexanoate only led to very low conversion of 4-methylbenzaldehyde into 4-methylbenzoic acid in the absence of $VO(acac)_2$ (see Table 2, entry 10). It has to be mentioned that copper salts have been widely reported as oxygen-activating cocatalysts: see (a) Tsuji, J. *Synthesis* **1984**, 369. (b) Lorber, C. Y.; Smidt, S. P.; Osborn, J. A. *Eur. J. Inorg. Chem.* **2000**, 655. (c) Muldoon, J.; Brown, S. N. *Org. Lett.* **2002**, *4*, 462.

[15] Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cirney, J.; Eckert, C. A.; Frederick, W. J.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T. *Science* **2006**, *311*, 484.

TABLE 2. Aerobic Oxidation of Alcohols into Acids or Aldehydes in Ionic Liquids[g]

entry	alcohols	product	time (h)	condition[a]	yield (%)[b]
1	 **1a**	 **2a**	12	A	94
		 **3a**	24	B	83
2	 **1b**	 **2b**	8	A	90
			8	A	84[c]
		 **3b**	12	B	89
			20	B	87[c]
3	 **1c**	 **2c**	12	A	86
		 **3c**	24	B	82
4	 **1d**	 **2d**	12	A	86
		 **3d**	24	B	93
5	 **1e**	 **2e**	8	A	91
		 **3e**	24	B	87
6	 **1f**	 **2f**	12	A	80
		 **3f**	24	B	73
7	 **1g**	 **2g**	12	A	85[d]
		 **3g**	24	B	56[d]
8	 **1h**	 **2h**	12	A	81
		 **3h**	24	B	67
9	 **1i**	 **2i**	24	A	-[d,e]
		 **3i**	24	B	-[d,e]
10	 **2e**	 **3e**	12 12	B B	80 (11)[f,g]
11	 **1j**	 **2j**	12	A	76[d]
		 **3j**	24	B	17[d]
12	 **1k**	 **4**	24	A	83[d]

[a] Reaction conditions A: 2 mmol alcohol, 2 mol % VO(acac)$_2$, 6 mol % DABCO, 1 atm O$_2$, 0.30 g of [bmim]PF$_6$, 95 °C for the specific time; reaction conditions B: 2 mmol alcohol, 2 mol % VO(acac)$_2$, 2 mol % Cu(II) 2-ethylhexanoate, 6 mol % DABCO, 1 atm O$_2$, 0.30 g of [hmim]OTf, 95 °C for the specific time. [b] Isolated yield by flash chromatography. [c] Reaction was run in 100 mmol scale in 10.0 g of ionic liquid at 95 °C for the specific time. [d] 4 mol % VO(acac)$_2$ was used. [e] The reaction was run at 110 °C. [f] No VO(acac)$_2$ was added. [g] Determined by ^{1}H NMR analysis of the crude reaction mixture.

zylic alcohol turned out to be readily oxidized into aldehyde in good isolated yield, its oxidation into acid proved to be inefficient with the acid only as minor product after 24 h (17% isolated yield, Table 2, entry 11). Furthermore, 1-(3,4-dimethoxyphenyl)ethanol could be successfully oxidized into the ketone, which coincided with our previous observation that secondary benzylic and allylic alcohols could be oxidized into the corresponding ketones.[11]

Next, we examined the recyclability of the two catalytic systems for aerobic oxidation of benzyl alcohol in ionic liquids (Table 3). The recovery and reuse of both the catalytic systems was accomplished after full extraction of benzaldehyde or benzoic acid with ether. It is important to stress that the catalytic

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(16) It has to be mentioned that the lignin model compound, coniferyl alcohol (4-hydroxy-3-methoxycinnamyl alcohol) has also been tested for the aerobic oxidation without success.

systems were easy to handle and proved to be readily recyclable for two additional runs with only slight drop in activity.

In conclusion, selective aerobic oxidation of activated primary alcohols into acids or aldehydes has been achieved in ionic liquids. The catalytic systems show good compatibility with heteroatom-containing (S and N) substrates. Furthermore, both copper complexes and the ionic liquids play crucial roles in the product selectivity. Most importantly, the catalysts are easy to handle and could be recycled and reused for three runs without any significant loss of catalytic activity.

Experimental Section

General Procedure for Catalytic Aerobic Oxidation of Alcohols into Aldehydes in [bmim]PF_6. Into a 16-mL vial was added a mixture of alcohol (2 mmol), vanadyl acetylacetonate ($VO(acac)_2$, 10.6 mg, 0.04 mmol), 1,4-diazabicyclo[2,2,2]octane (DABCO, 13.4 mg, 0.12 mmol), and 0.30 g [bmim]PF_6. The vial was capped with a rubber septum, and the reaction mixture was stirred at 95 °C under 1 atm O_2 (around 3 bubble/s by a needle through the rubber septum and vented through a mineral oil bubbler) for the specific time, and then extracted with ethyl ether (3 × 3 mL). The combined ether phase was concentrated in vacuo. The residue was purified by flash chromatography (*n*-pentane/diethyl ether = 8:1) to afford aldehyde.

General Procedure for Catalytic Aerobic Oxidation of Alcohols into Acids in [hmim]OTf. Into a 16-mL vial was added a mixture of alcohol (2 mmol), vanadyl acetylacetonate ($VO(acac)_2$, 10.6 mg, 0.04 mmol), copper (II) 2-ethylhexanoate (14.0 mg, 0.04 mmol), 1,4-diazabicyclo[2,2,2]octane (DABCO, 13.4 mg, 0.12 mmol), and 0.30 g of [hmim]OTf. The vial was capped with a rubber septum, and the reaction mixture was vigorously stirred at 95 °C under 1 atm O_2 (around 3 bubble/s by a needle through the rubber septum and vented through a mineral oil bubbler) for the specific time, and then extracted with ethyl ether (3 × 5 mL). The combined ether phase was concentrated in vacuo. The residue was purified by flash chromatography (*n*-pentane/diethyl ether = 2:1) to afford the acid.

General Procedure for Recycling of the Catalytic System for Aerobic Oxidation of Benzyl Alcohol into Benzaldehyde. A mixture of benzyl alcohol (216 mg, 2 mmol), vanadyl acetylacetonate ($VO(acac)_2$, 10.6 mg, 0.04 mmol), and 1,4-diazabicyclo[2,2,2]octane (DABCO, 13.4 mg, 0.12 mmol) in 0.30 g of ionic liquid [bmim]PF_6 was stirred at 95 °C under 1 atm O_2 (around 3 bubble/s by a needle through the rubber septum and vented through a mineral oil bubbler) for 8 h, and then extracted with ethyl ether (3 × 3 mL). The combined ether phase was concentrated in vacuo. The residue was purified by flash chromatography to afford benzaldehyde. The next run was performed by adding fresh benzyl alcohol (2 mmol) to the catalytic system under the same experimental conditions for the specific reaction time (see Table 3 for the reaction time).

TABLE 3. Recycling of the Catalytic Systems for the Aerobic Oxidation of Benzyl Alcohol

$$\underset{\mathbf{2b}}{\mathrm{PhCHO}} \xleftarrow{\text{conditions A}} \underset{\mathbf{1b}}{\mathrm{PhCH_2OH}} \xrightarrow{\text{conditions B}} \underset{\mathbf{3b}}{\mathrm{PhCO_2H}}$$

			yield (%)[b]	
run	time h	conditions[a]	**2b**	**3b**
1	8	A	90	
	12	B		89
2	8	A	84	
	12	B		88
3	10	A	83	
	15	B		76

[a] Reaction conditions A: 2 mmol 4-benzyl alcohol, 2 mol % $VO(acac)_2$, 6 mol % DABCO, 1 atm O_2, 0.30 g of [bmim]PF_6, 95 °C for the specific time; reaction conditions B: 2 mmol benzyl alcohol, 2 mol % $VO(acac)_2$, 2 mol % Cu(II) 2-ethylhexanoate, 6 mol % DABCO, 1 atm O_2, 0.30 g of [hmim]OTf, 95 °C for the specific time. [b] Isolated yield by flash chromatography.

General Procedure for Recycling of the Catalytic System for Aerobic Oxidation of Benzyl Alcohol into Benzoic Acid. A mixture of benzyl alcohol (216 mg, 2 mmol), vanadyl acetylacetonate ($VO(acac)_2$, 10.6 mg, 0.04 mmol), copper (II) 2-ethylhexanoate (14.0 mg, 0.04 mmol), and 1,4-diazabicyclo[2,2,2]octane (DABCO, 13.4 mg, 0.12 mmol) in 0.30 g ionic liquid [hmim]OTf was vigorously stirred at 95 °C under 1 atm O_2 (around 3 bubble/s by a needle through the rubber septum and vented through a mineral oil bubbler) for 12 h, and then extracted with ethyl ether (3 × 5 mL). The combined ether phase was concentrated in vacuo. The residue was purified by flash chromatography to afford benzoic acid. The next run was performed by adding fresh benzyl alcohol (2 mmol) to the catalytic system under the same experimental conditions for the specific reaction time (see Table 3 for the reaction time).

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Supporting Information Available: ^1H and ^{13}C NMR data and ^1H NMR spectra for all isolated products. This material is available free of charge via the Internet at http://pubs.acs.org.

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