

# Environmentally Friendly Oxidation of Alcohols with Hydrogen Peroxide Catalyzed by Sodium Tungstate and Acidic Ionic Liquids

LANG Xian-jun<sup>1, 2</sup>, LI Zhen<sup>1</sup>, XIA Chun-gu<sup>1 \*</sup>

(1. *State key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China;*

2. *Graduate University of Chinese Academy of Sciences, Beijing 100049, China)*

**Key words:** Alcohol oxidation; Sodium tungstate; Ionic liquid; Hydrogen peroxide

**CLC number:** O643.32

**Document code:** A

Oxidation of alcohols to the corresponding carbonyl compounds is one of the fundamental functional group transformations in organic synthesis<sup>[1]</sup>. Generally, these reactions require stoichiometric amounts of inorganic/organic oxidants, toxic or hazardous oxidizing agents<sup>[2]</sup>. Environmentally benign and sustainable transformations in organic chemistry are now considered to be basic goals and requirements in the development of modern organic syntheses. Oxidation processes present the most formidable ensemble of challenges to green yet viable operations. One challenge is to use the most environmentally and economically attractive oxidants<sup>[3]</sup>. Therefore, it is not surprising that in the arena of oxidative transformations one major goal is the replacement of stoichiometric procedure with catalytic procedures using environmentally benign oxidant. So the selective catalytic oxidation of organic compounds with a "green" and atom efficient oxidant, aqueous H<sub>2</sub>O<sub>2</sub>, is highly desirable<sup>[4]</sup>.

Many tungsten and molybdenum containing catalytic protocols are available in the liquid phase oxidation of alcohols with aqueous H<sub>2</sub>O<sub>2</sub><sup>[5]</sup>. One of the simple and efficient system was reported by Sato et al in

which alcohols could be efficiently oxidized to corresponding carbonyl compounds with 30% H<sub>2</sub>O<sub>2</sub> catalyzed by Na<sub>2</sub>WO<sub>4</sub> and a phase transfer catalyst, [CH<sub>3</sub>(n - C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>N]HSO<sub>4</sub><sup>[6]</sup>. However, the phase transfer catalyst is soluble in the organic phase. It is not avoidable to have the drawback of difficult catalyst/product separation.

Over the past few decades, there has been an explosion of the use of ionic liquids in a wide range of catalytic and stoichiometric reactions as well as in many other applications<sup>[7]</sup>. Recently much attention is paid to the organic reaction in or facilitated with ionic liquids<sup>[8]</sup>. Previously, we reported that 12 - phosphotungstic acid in conjunction with acidic ionic liquids was efficient oxidation catalyst for clean synthesis of adipic acid<sup>[9]</sup>. In continuation of our research to develop new oxidation catalyst system with tungsten complex and ionic liquids, herein, we report an efficient green catalytic process for oxidation of alcohols with 30% H<sub>2</sub>O<sub>2</sub> catalyzed by Na<sub>2</sub>WO<sub>4</sub> · 2H<sub>2</sub>O in combination with acidic ionic liquids under organic solvent free conditions. Apart from the green nature of this system, the catalyst can be recycled without apparent loss of cata-

**Received date:** 2007-10-09; **revised date:** 2007-11-20.

**Foundation item:** Funded by NSFC (No. 20373082 and No. 20625308).

**Biography:** Lang Xian-jun, male, born in December 1982, M. Sc. Candidate.

\* E-mail: cgxia@lzb.ac.cn.

lytic activity by simple post – reaction treatment which makes it a technically and commercially alternative for the future application.

## 1. Experimental

### 1.1 Materials and equipments

30%  $\text{H}_2\text{O}_2$  etc. inorganic materials were purchased from National Pharmaceuticals Group (Shanghai). Organic reagents were supplied by Acros Organics. All the reagents were of analytical grade and used without further purification.

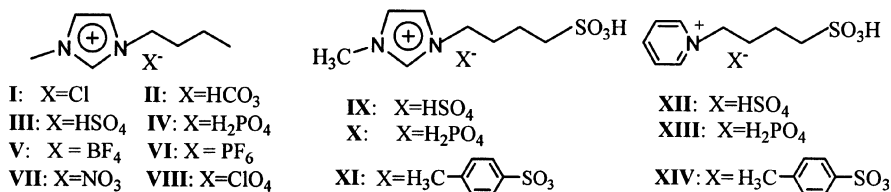


Fig. 1 Ionic liquids used in this paper

Abbreviations: I [Bmim]Cl; II [Bmim][ $\text{HCO}_3$ ]; III [Bmim][ $\text{HSO}_4$ ]; IV [Bmim][ $\text{H}_2\text{PO}_4$ ];

V [Bmim][ $\text{BF}_4$ ]; VI [Bmim][ $\text{PF}_6$ ]; VII [Bmim][ $\text{NO}_3$ ]; VIII [Bmim][ $\text{ClO}_4$ ];

IX [(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>HMim][ $\text{HSO}_4$ ]; X [(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>HMim][ $\text{H}_2\text{PO}_4$ ]; XI [(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>HMim][Tos];

XII [(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>HPy][ $\text{HSO}_4$ ]; XIII [(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>HPy][ $\text{H}_2\text{PO}_4$ ]; XIV [(CH<sub>2</sub>)<sub>4</sub>SO<sub>3</sub>HPy][Tos]

in this study were synthesized according to literature procedure<sup>[10]</sup>. Some ionic liquids were prepared with slight modification if needed and the products were confirmed by NMR and IR.

### 1.3 General procedure for the alcohol oxidation

A 100 mL round bottom flask equipped with a condenser was charged with  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  (0.5 mmol), ionic liquid (0.5 mmol), cyclohexanol (75 mmol) and  $\text{H}_2\text{O}$  (15 mL). After vigorous stirring (1000 rpm) for 10 min at 363K, the reaction was initiated by adding 112.5 mmol  $\text{H}_2\text{O}_2$  (12.75 mL 30% aqueous  $\text{H}_2\text{O}_2$ ). The mixture was kept at this temperature for 8 h, and then cooled to room temperature. The oxidation products were extracted with ethyl acetate and quantified with GC.

## 2 Results and discussion

Cyclohexanol was chosen as the probe substrate to investigate the effects of various ionic liquids on the transformation of cyclohexanol to cyclohexanone when 30%  $\text{H}_2\text{O}_2$  was used as oxidant. The results obtained are summarized in Table 1. Those results indicate that

The oxidation products were determined by GC/MS (HP 6890/5973) and quantitative analyses were performed on GC (Agilent 6820) with a flame ionization detector and SE – 54 capillary column and with  $\text{N}_2$  carrier gas and decane was used as the internal reference. NMR studies were carried out on an INOVA – 400 MHz spectrometer. FTIR spectra (KBr disks) were obtained on a Bruker IFS 120HR FT – IR spectrometer.

### 1.2 Preparation for the ionic liquids

Room temperature ionic liquids (Figure 1) used

ionic liquids play an important role in the catalytic oxidation process. Without addition of any ionic liquids described in Figure 1, the yield of product is rather low (entry 1). After ionic liquids addition, the yields of entries 2, 3, 8 and 9 show slight increases compared with entry 1, which might attribute to, if so, the phase transfer function of the cation part of the ionic liquids since the present system comprises two immiscible liquid phase. The results of entries 6 and 7 are better than entries 2, 3, 8 and 9. That might be caused by the acidic nature of those two ionic liquids since the acidity is essential in the catalytic system<sup>[11]</sup>. Note that the intrinsic physicochemical properties of [Bmim][ $\text{PF}_6$ ] and [Bmim][ $\text{BF}_4$ ] are quite different, such as, [Bmim][ $\text{PF}_6$ ] is hydrophobic, whereas [Bmim][ $\text{BF}_4$ ] is hydrophilic, so that [Bmim][ $\text{BF}_4$ ] can adjust the pH value of the water phase better. That might be the reason why the yield of entry 6 is higher than that of entry 7. The other acidic ionic liquids based upon the 1 – n – butyl – 3 – methylimidazolium cation (entries 4 and 5) can boost the yields of cyclohexanone more apparently than [Bmim][ $\text{PF}_6$ ] and

Table 1 Effects of ionic liquids on oxidation of cyclohexanol

Entry	Ionic Liquid	Conversion ( % )	Yield ( % )	TON
1	—	5.57	5.4	8.36
2	[ Bmim ] Cl	16.73	15.34	23.01
3	[ Bmim ] [ HCO <sub>3</sub> ]	27.14	25.51	38.26
4	[ Bmim ] [ HSO <sub>4</sub> ]	75.65	73.63	110.00
5	[ Bmim ] [ H <sub>2</sub> PO <sub>4</sub> ]	78.52	77.31	116.71
6	[ Bmim ] [ BF <sub>4</sub> ]	55.92	53.54	80.31
7	[ Bmim ] [ PF <sub>6</sub> ]	45.08	43.92	65.88
8	[ Bmim ] [ NO <sub>3</sub> ]	16.28	15.30	22.92
9	[ Bmim ] [ ClO <sub>4</sub> ]	16.79	15.78	23.67
10	[ ( CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HMim ] [ HSO <sub>4</sub> ]	82.24	81.11	121.67
11	[ ( CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HMim ] [ H <sub>2</sub> PO <sub>4</sub> ]	89.23	87.51	131.27
12	[ ( CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HMim ] [ Tos ]	84.74	83.07	124.61
13	[ ( CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HPy ] [ HSO <sub>4</sub> ]	86.63	84.43	126.64
14	[ ( CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HPy ] [ H <sub>2</sub> PO <sub>4</sub> ]	85.61	83.76	125.64
15	[ ( CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HPy ] [ Tos ]	86.80	83.33	125.00

Reaction conditions: substrate (75 mmol), H<sub>2</sub>O<sub>2</sub> (112.5 mmol) Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (0.5 mmol), ionic liquid (0.5 mmol), H<sub>2</sub>O (15 mL), 363 K, 8 h

[ Bmim ] [ BF<sub>4</sub> ]. That may partly ascribe to their stronger acidity. The other reason may be due to the in situ generation of catalytic active intermediates of [ SO<sub>4</sub> W<sub>2</sub>O<sub>2</sub>( μ - O<sub>2</sub> )<sub>2</sub>( O<sub>2</sub> )<sub>2</sub> ]<sup>2-</sup> and [ PO<sub>4</sub> W<sub>2</sub>O<sub>2</sub>( μ - O<sub>2</sub> )<sub>2</sub>( O<sub>2</sub> )<sub>2</sub> ]<sup>3-</sup> originated from HSO<sub>4</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and Na<sub>2</sub>WO<sub>4</sub> · 2H<sub>2</sub>O in the presence of H<sub>2</sub>O<sub>2</sub><sup>[12]</sup>. The sulfonyl - functionalized task specific ionic liquids ( entries 10 ~ 15 ) are usually used in acidic catalysis. Here we discover that they can be used in oxidation catalysis in combination with Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O with higher efficiency than [ Bmim ] [ HSO<sub>4</sub> ] and [ Bmim ] [ H<sub>2</sub>PO<sub>4</sub> ]. The yields of those 6 kinds of ionic liquids are quite similar. [ ( CH<sub>2</sub> )<sub>4</sub>SO<sub>3</sub>HMim ] [ H<sub>2</sub>PO<sub>4</sub> ] gave the best results. Apart from the aforementioned reason, other unclear effects may determine the dissimilar activities of different ionic liquids. Further work should be done to understand the current catalyst system well. The mechanism of this catalytic oxidation system is in progress now.

As always in research involving in catalysis, attention must be paid to the vital issue of catalyst integ-

riety, recovery and recycling. As Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O and [ ( CH<sub>2</sub> )<sub>4</sub>SO<sub>3</sub>HMim ] [ H<sub>2</sub>PO<sub>4</sub> ] gave the best catalytic result, we selected them to investigate the reusability of this catalyst system. Recycle experiments were carried out with cyclohexanol oxidation as the model reaction. After completion of the reaction, the product and unreacted substrate, if any, were extracted with ethyl acetate for several times. Under the present reaction conditions, since the amount of H<sub>2</sub>O<sub>2</sub> was in excess, there should be some tungsten peroxide complex mentioned above or other species which were not clear yet in the solution. So it was washed several times with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> to decompose the remaining H<sub>2</sub>O<sub>2</sub>. Na<sub>2</sub>WO<sub>4</sub> and ionic liquid retain in water. After evaporation of water accompanied with the addition of aqueous H<sub>2</sub>O<sub>2</sub>, the recycle reaction was carried out in a procedure described in the experimental part with the catalyst imbedded in water. From table 2, we can see that even after 5 catalytic cycles, there was no apparent loss of catalytic activity. To sum up, it established the reusability of the catalyst system.

**Table 2 Recycle of the catalyst for the oxidation of cyclohexanol**

Round	Yield ( % )
1	87. 51
2	85. 89
3	86. 36
4	84. 49
5	84. 75

Reactions were carried out under the same conditions as Table 1.

**Table 3 Oxidation of Various Alcohols catalyzed by Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O and [ ( CH<sub>2</sub> )<sub>4</sub>SO<sub>3</sub>HMim][ H<sub>2</sub>PO<sub>4</sub> ] at 363 K**

Entry	Substrate	Conversion ( % )	Substrate/H <sub>2</sub> O <sub>2</sub> <sup>a</sup>	Product ( Selectivity, mol% )	Time ( h )
1	2 – propano	1 ~ 100	2/3	acetone (99.1)	8
2	2 – butanol	~ 100	2/3	butanone (99.3)	8
3	2 – pentanol	55. 4	2/3	2 – pentanone (96.0)	8
4	3 – pentanol	53. 1	2/3	diethyl ketone (94.5)	8
5	sec – phenylethanol	100	2/3	acetophenone (100)	8
6	diphenyl carbinol	69. 8	2/3	diphenyl ketone (100)	8
7	benzyl alcohol	87. 2	1/3	benzaldehyde (52.4) benzoic acid (39.2)	8
8	benzyl alcohol	100	1/4	benzoic acid (95.2)	12
9	1 – hexanol	2. 9	1/4	hexanal (100)	12
10	1 – octanol	1. 0	1/4	octanal (100)	12

Reactions were carried out under the same conditions as Table 1. <sup>a</sup> molar ratio

the conversion and selectivity of benzoic acid increased evidently to achieve 100% and 95.2% respectively. Compared with primary aromatic alcohol, the results for the oxidation of primary aliphatic alcohols were not satisfactory. Even 4.0 equivalents of H<sub>2</sub>O<sub>2</sub> were charged and the reaction time was 12 h, the conversions were very low (entries 9 and 10). Interestingly, their selectivity to corresponding aldehydes was 100%.

3 Conclusions

In summary, we utilize commercially available sodium tungstate and acidic ionic liquids to develop an efficient catalyst system for oxidation of a variety of primary and secondary alcohols with H<sub>2</sub>O<sub>2</sub> at 363K. The present catalytic system is inexpensive, easy to handle

Having obtained these results, the scope of this catalyst system for alcohol oxidation was surveyed for a range of substrates (Table 3). Oxidation of secondary alcohols afforded the corresponding ketones in excellent (entries 1, 2 and 5) and medium (entries 3, 4 and 6) yields. The oxidation of the benzyl alcohol (entry 7) with 3.0 equivalents of H<sub>2</sub>O<sub>2</sub> afforded benzaldehyde, benzoic acid and small amount of benzyl benzoate. Whereas when 4.0 equivalents of H<sub>2</sub>O<sub>2</sub> was used and the reaction time prolonged for another 4 h (entry 8),

and environmentally benign. In addition, it is reusable and exhibits consistent activity upon recycling.

References:

[1] Hudlicky M. Oxidations in Organic Chemistry [M]. ACS, Washington, DC. 1990

[2] Sheldon R A, Arends I W C E, Dijkman A. *Catal. Today*[J], 2000, **57**: 157 ~ 166

[3] Hill C L. *Angew. Chem. Int. Ed.* [J], 2004, **43**: 402 ~ 404

[4] Jones C W, Applications of Hydrogen Peroxide and Derivatives [M]. RSC, Cambridge, 1999

[5] Noyori R, Aoki M, Sato K. *Chem. Commun.* [J], 2003, 1977 ~ 1986

[6] Sato K, Aoki M, Takai J, *et al.*, *J. Am. Chem. Soc.* [J], 1997, **119**: 12 386 ~ 12 387

[7] a Parvulescu V I, Hardacre C. *Chem. Rev.* [J], 2007,

107: 2 615 ~2 665  
b Shao Li-li(邵丽丽), Wang Wen-juan(王雯娟), Peng Hui-qi(彭惠琦), *et al.* *J. Mol. Catal.* (China)(分子催化)[J], 2007, **21**(6): 520 ~ 524  
c Xin Jia-ying(辛嘉英), Zhao Yong-jie(赵永杰), Xia Chun-gu(夏春谷), *et al.* *J. Mol. Catal.* (China)(分子催化)[J], 2006, **20**(1): 76 ~ 83

[8] Wasserscheid P, Welton T. *Ionic Liquids in Synthesis* [M]. Wiley, Weinheim, 2002

[9] Lu Rui-ling(路瑞玲), Li Zhen(李臻), Chen Jing(陈静), Lang Xian-jun(郎贤军). *J. Mol. Catal.* (分子催化)(China)[J], 2007, **21**: 268 ~ 271

[10] Gui J, Liu D, Cong X, *et al.*, *J. Chem. Res.* [J], 2005, 520 ~ 522

[11] Sato K, Aoki M, Takagi J. *Bull. Chem. Soc. Jpn.* [J], 1999, **72**: 2 287 ~ 2 306

[12] Brégeault J M, Vennat M, Salles L, *et al.*, *J. Mol. Catal. A: Chem.* [J], 2006, **250**: 177 ~ 189

# 钨酸钠与酸性离子液体催化醇的环境友好氧化反应

郎贤军<sup>1, 2</sup>, 李臻<sup>1</sup>, 夏春谷<sup>1\*</sup>

(1. 中国科学院兰州化学物理研究所 羰基合成与选择氧化国家重点实验室, 甘肃 兰州 730000;  
2 中国科学院研究生院, 北京 100049)

**摘 要:**钨酸钠与酸性离子液体组成的催化体系可以催化双氧水进行醇的清洁氧化,反应在有机底物/水两相中进行. 本体系在催化氧化仲醇为相应的酮时具有很好的活性;催化伯醇氧化时可以得到相应的醛、羧酸或两者的混合物. 整个催化体系具有很好的重复利用性.

**关 键 词:**醇的氧化;钨酸钠;离子液体;双氧水