Received: February 26, 2014 | Accepted: March 19, 2014 | Web Released: March 26, 2014 CL-140159

Baeyer–Villiger Oxidation of Cyclic Ketones Using Aqueous Hydrogen Peroxide Catalyzed by Potassium Salts of Tungstophosphoric Acid

Qingguo Ma, Wanzhen Xing, Junhui Xu, and Xinhua Peng*
School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, P. R. China

(E-mail: xhpeng@mail.njust.edu.cn)

The salts of 12-tungstophosphoric acid catalysts are prepared with varying potassium content. The resulting catalysts are active for the Baeyer–Villiger oxidation of cyclic ketones with 30 wt % H_2O_2 and achieve good conversions and yields. KHPW is the preferred catalyst in the reaction because of its reusability and environmental benefits.

The Baeyer–Villiger oxidation of ketones is a reaction of major interest with regard to syntheses in organic chemistry with a large range of possible applications spanning diverse areas such as syntheses of antibiotics and steroids, pheromones for agrochemistry, and monomers for polymerization.[1] However, the traditional Baeyer–Villiger reaction is carried out with various peroxyacids; the performance of this process on an industrial scale is associated with some technological problems caused by the necessity of synthesis and isolation of peroxyacids.[2]

Two alternative oxidants, molecular oxygen[3] and aqueous hydrogen peroxide,[4] have been used in the Baeyer–Villiger reaction to solve some environmental problems. When molecular oxygen and aqueous hydrogen peroxide are used as oxidizing agents, catalysts are required for the active transfer of oxygen from the oxidizer to the substrate. Low-concentration aqueous hydrogen peroxide is a promising oxidant for the Baeyer–Villiger reaction, because hydrogen peroxide is converted into environmentally benign water.[5] An efficient catalytic system comprising Sn–zeolites was used by Corma et al. for the Baeyer–Villiger reaction of cycloketones with aqueous hydrogen peroxide.[6] Recently, much effort has been devoted to finding other effective catalysts to activate the reagent. Reported examples include Sn–clay,[7] Sn-MWW,[8] β-zeolite,[9] pillared clays,[10] MCM-41,[11] hydrotalcite,[12] Sn(salen)–NaY zeolite,[13] and TS-1.[14] When these catalysts are used, high temperature is required to activate the reagent. While many studies on finding effective catalysts to activate the reagent have been reported until now,[8,9,15] the study on the oxidation of cycloketones using low concentration of aqueous hydrogen peroxide and solid acids is lacking. 12-Tungstophosphoric acid (HPW) is an inorganic solid acid. Its acid strength is higher than that of conventional solid acids;[16] however, it is not efficient because of its high solubility in polar media. Generally, the incorporation of alkaline metals into 12-tungstophosphoric acid can enhance its water tolerance and simultaneously adjust acidity.[17] In view of this, we attempt to synthesize lactones by using the salts of 12-tungstophosphoric acid.

All chemicals are analytical grade without further purification. The structures of tungstophosphoric acid and its potassium salts are characterized by IR spectroscopy (Nicolet FTIR IS10) and X-ray diffractometer (Rigaku MiniFlex 600). Thermogravimetric analysis of tungstophosphoric acid and its potassium salts are performed using a TGA/SDTA851e instrument under a nitrogen flow of 5 mL min^{-1}. Samples (3 mg) are heated from 50 to 800 °C at a rate of 10 °C min^{-1}. GC (Shimadzu GC-2014C) is used to determine the product composition.

The salts of 12-tungstophosphoric acid catalysts are prepared with varying potassium content. In a typical method, the required amount of HPW is dissolved in distilled water and a calculated amount of K_2CO_3 is added dropwise to this solution at a rate of 0.1 mL min^{-1} with vigorous stirring at room temperature. HPW and K_2CO_3 are used after pretreatment at 423 K in vacuum. The resultant mixture is stirred for 3 h, and a white solid is precipitated and separated by filtration from the resultant mixture. Prior to use, these salts are pretreated at 423 K in vacuum for 2 h. These salts are denoted as KPW (the quantity of K in KPW is 3.9 wt %) and KHPW (the quantity of K in KHPW is 1.3 wt %).

The typical procedure for the oxidation of 2-heptylcyclopentanone is as follows. KHPW (25 mg) and 2-heptylcyclopentanone (2.5 mmol, 450 mg) are mixed and the oxidizing agent, aqueous hydrogen peroxide (30 wt %; 6.2 mmol), is slowly added dropwise to this mixture with stirring at 40 °C. The resultant mixture is stirred for 12 h. The catalyst is separated by filtration. The aqueous phase is removed from the filtration. Conversion of 2-heptylcyclopentanone and selectivity of δ-dodecalactone are determined by quantitative GC analyses of the organic phase. The organic phase is evaporated under reduced pressure and further purified by column chromatography over silica gel using 1:5 ethyl acetate–hexane as the eluent to furnish pure δ-dodecalactone.

The FT-IR spectra of HPW and KHPW are displayed in Figure 1. The spectrum of HPW contains vibration bands characteristic of the Keggin anion: 1080, 990, 890, and 810 cm^{-1}, corresponding to vibrations P–O_a, W–O_d, W–O_b–W, and W–O_c–W, respectively (O_a: oxygen in the central PO_4 tetrahedron, O_d: terminal oxygen bonding to W atom, O_b:

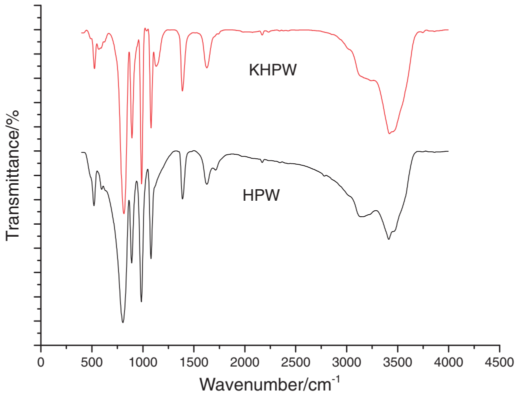


Figure 1. FT-IR spectra of HPW and KHPW.

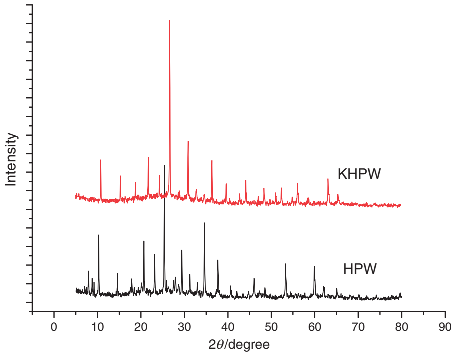


Figure 2. XRD patterns of HPW and KHPW.

edge-sharing oxygen connecting W, and O_c: corner-sharing oxygen connecting W_3O_{13} units).[18] These bands also appear in the spectrum of KHPW and their positions are not changed relative to those in the spectrum of HPW. This indicates that the structures of the Keggin anions of HPW are preserved when protons are replaced by potassium ions.

The XRD patterns of HPW and KHPW are shown in Figure 2. The XRD pattern of KHPW is similar to that of HPW and only slightly shifted in comparison to that of HPW toward higher angles. Thus, we conclude that KHPW is formed.

Thermal stability is measured mainly by TGA. Figure 3 shows the TGA curves for HPW and KHPW. For HPW, three weight loss regions can be observed at 58–100, 100–250, and 330–415 °C on the TGA curve. Similarly, for KHPW, a small weight loss region is found from 65 to 120 °C, and a larger one is found from 330 to 360 °C. The acid form of HPW is usually obtained with small amounts of physically adsorbed water and large amounts of crystal water, and most of these water molecules are released below 250 °C. The weight loss at 330–415 °C is probably due to the decomposition of HPW. KHPW is only obtained with small amounts of physically adsorbed water; the weight loss due to decomposition is decreased because of the replacement of protons.

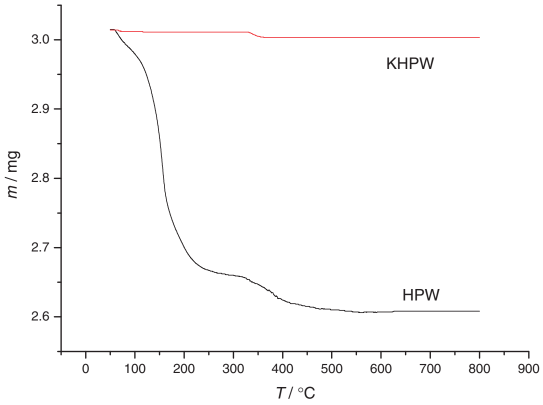


Figure 3. TGA curves for HPW and KHPW.

Table 1. Catalytic performance of various catalysts for the oxidation of 2-heptylcyclopentanone with H_2O_2[a]

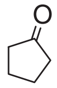
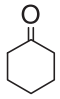
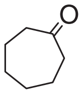
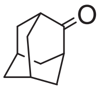
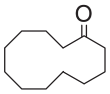
Catalyst	Time/h	Conversion/%[b]	Yield/%[c]
—	24	trace	trace
HPW	10	97	67
H-ZSM-5	24	11	8
HY zeolite	24	9	7
KPW	24	trace	trace
KHPW	24	74	49
KHPW[d]	18	98	72
KHPW[e]	12	98	81
KHPW[e]	18	98	68
KHPW[f]	8	98	70
KHPW[e,g]	12	98	81
KHPW[e,h]	12	95	76
KHPW[e,i]	12	92	73
KHPW[e,j]	12	11	7

[a] Reaction conditions: 2-heptylcyclopentanone (2.5 mmol), catalysts (25 mg), experiments performed at 40 °C, aqueous hydrogen peroxide (30 wt %) (6.25 mmol). [b] Calculated by GC. [c] Isolated yield. [d] 50 mg. [e] 100 mg. [f] 150 mg. [g] 1st recycled. [h] 2nd recycled. [i] 3rd recycled. [j] KHPW is filtered out after 1 h.

A series of catalysts are studied using H_2O_2 as an oxidant to produce δ-dodecalactone under the same reaction conditions. The results of this study are summarized in Table 1. In the absence of a catalyst, 2-heptylcyclopentanone is difficult to react with H_2O_2 to produce δ-dodecalactone. In the homogeneous case, the HPW catalyst results in quite high conversion of 2-heptylcyclopentanone because of its strong acidity and high solubility in the liquid phase. Leaching of HPW is a common problem in reactions. The use of several other insoluble solid acids (H-ZSM-5, HY zeolite, KPW, and KHPW) instead of HPW slows the reaction considerably under heterogeneous conditions; especially, when using KPW as a catalyst, the conversion of 2-heptylcyclopentanone is rather poor. It proves that the catalytic activity is close to that of protons. Increasing the amount of KHPW under this condition causes a significant increase of the conversion of 2-heptylcyclopentanone and yield of δ-dodecalactone. A further increase of the conversion rate of 2-heptylcyclopentanone is observed by increasing the amount of KHPW, but an excess amount has a strong negative impact on selectivity. It can be seen that δ-dodecalactone is an unstable product, where 5-oxododecanoic acid is present as a by-product. Indeed, 5-oxododecanoic acid is formed by the oxidation of 5-hydroxydodecanoic acid, which is formed by the hydrolysis of δ-dodecalactone with water present in the reaction media. The amount of KHPW affects the oxidation rate of 2-heptylcyclopentanone and the selectivity of δ-dodecalactone; it seems that very large amounts of KHPW can also accelerate the hydrolysis and oxidation of δ-dodecalactone. The appropriate amount of KHPW is 100 mg. The catalyst is repeatedly isolated by filtration, washed with ethyl acetate for 1 h to remove organic compounds, and used again in the reaction without further treatment. The results suggest that the KHPW catalyst can be recycled.

Table 2 summarizes the reaction of simple cyclic ketones in the presence of KHPW. The yields of lactones depend on the sizes of the rings. In the case of 2-adamantanone and cyclododecanone, the corresponding lactones are obtained in good yields. Despite high conversions achieved for cyclopentanone, cyclohexanone, and cycloheptanone, the yields of corresponding lactones are low; this is tentatively ascribed to the hydrolysis of lactones.

Table 2. Oxidation of cyclic ketones to give corresponding lactones[a]

Substrate	Temperature/°C	Time/h	Conversion/%[b]	Yield/%[b]
	15	24	91	42
	40	24	95	46
	55	24	89	37
	40	12	98	95
	55	24	93	82

[a]Reaction conditions: Substrate (2.5 mmol), catalyst/substrate = 20 wt %, aqueous hydrogen peroxide (30 wt %) (6.25 mmol), dioxane (3.5 mL). [b]Calculated by GC.

The excellent behavior of KHPW for the oxidation of cyclic ketones suggests a possible reaction process. First, the cyclic ketone is protonated by KHPW to activate the carbonyl group. Subsequently, hydrogen peroxide attacks the more electrophilic carbonyl carbon atom. After a rearrangement step, the lactone is replaced by a new substrate molecule.

A comparison of several acid catalysts shows that KHPW is an environmentally benign catalyst for the transformation of 2-heptylcyclopentanone to δ-dodecalactone without the use of organic solvents or highly concentrated hydrogen peroxide. Although the yields of lactones obtained by the reactions catalyzed by KHPW are different, this is a useful method for the Baeyer–Villiger oxidation of cyclic ketones.

This project was funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

References and Notes

1 S. Baj, A. Chrobok, R. Słupska, *Green Chem.* **2009**, *11*, 279.

2 R. A. Michelin, A. Sgarbossa, A. Scarso, G. Strukul, *Coord. Chem. Rev.* **2010**, *254*, 646; M. Uyanik, D. Nakashima, K. Ishihara, *Angew. Chem., Int. Ed.* **2012**, *51*, 9093; A. Cavarzan, A. Scarso, P. Sgarbossa, R. A. Michelin, G. Strukul, *ChemCatChem* **2010**, *2*, 1296; E.-Y. Jeong, M. B. Ansari, S.-E. Park, *ACS Catal.* **2011**, *1*, 855.

3 Y.-F. Li, M.-Q. Guo, S.-F. Yin, L. Chen, Y.-B. Zhou, R.-H. Qiu, C.-T. Au, *Carbon* **2013**, *55*, 269; Y. Nabae, H. Rokubuichi, M. Mikuni, Y. Kuang, T. Hayakawa, M.-a. Kakimoto, *ACS Catal.* **2013**, *3*, 230; Y. Imada, H. Iida, S.-i. Murahashi, T. Naota, *Angew. Chem., Int. Ed.* **2005**, *44*, 1704.

4 A. Corma, S. Iborra, M. Mifsud, M. Renz, *J. Catal.* **2005**, *234*, 96; S. Xu, Z. Wang, X. Zhang, X. Zhang, K. Ding, *Angew. Chem., Int. Ed.* **2008**, *47*, 2840; A. Yoshida, M. Yoshimura, K. Uehara, S. Hikichi, N. Mizuno, *Angew. Chem.* **2006**, *118*, 1990; L. M. D. R. S. Martins, E. C. B. A. Alegria, P. Smoleński, M. L. Kuznetsov, A. J. L. Pombeiro, *Inorg. Chem.* **2013**, *52*, 4534; A. Berkessel, M. R. M. Andreae, H. Schmickler, J. Lex, *Angew. Chem., Int. Ed.* **2002**, *41*, 4481.

5 Z.-w. Yang, L.-y. Niu, X.-j. Jia, Q.-x. Kang, Z.-h. Ma, Z.-g. Lei, *Catal. Commun.* **2011**, *12*, 798; J. M. Thomas, *Angew. Chem., Int. Ed.* **1999**, *38*, 3588; R. A. Michelin, E. Pizzo, A. Scarso, P. Sgarbossa, G. Strukul, A. Tassan, *Organometallics* **2005**, *24*, 1012.

6 A. Corma, L. T. Nemeth, M. Renz, S. Valencia, *Nature* **2001**, *412*, 423.

7 T. Hara, M. Hatakeyama, A. Kim, N. Ichikuni, S. Shimazu, *Green Chem.* **2012**, *14*, 771.

8 G. Liu, J.-G. Jiang, B. Yang, X. Fang, H. Xu, H. Peng, L. Xu, Y. Liu, P. Wu, *Microporous Mesoporous Mater.* **2013**, *165*, 210.

9 R. Ohno, K. Taniya, S. Tsuruya, Y. Ichihashi, S. Nishiyama, *Catal. Today* **2013**, *203*, 60.

10 L. S. Belaroui, A. B. Sorokin, F. Figueras, A. Bengueddach, J.-M. M. Millet, *C. R. Chim.* **2010**, *13*, 466.

11 A. Corma, M. T. Navarro, M. Renz, *J. Catal.* **2003**, *219*, 242.

12 U. R. Pillai, E. Sahle-Demessie, *J. Mol. Catal. A: Chem.* **2003**, *191*, 93.

13 B. Dutta, S. Jana, S. Bhunia, H. Honda, S. Koner, *Appl. Catal., A* **2010**, *382*, 90.

14 M. Sasidharan, A. Bhaumik, *J. Mol. Catal. A: Chem.* **2011**, *338*, 105.

15 A. Bhaumik, P. Kumar, R. Kumar, *Catal. Lett.* **1996**, *40*, 47; M. Paul, N. Pal, J. Mondal, M. Sasidharan, A. Bhaumik, *Chem. Eng. Sci.* **2012**, *71*, 564.

16 S. Zhu, X. Gao, Y. Zhu, Y. Zhu, X. Xiang, C. Hu, Y. Li, *Appl. Catal. B: Environ.* **2013**, *140–141*, 60; O. A. Kholdeeva, N. V. Maksimchuk, G. M. Maksimov, *Catal. Today* **2010**, *157*, 107.

17 A. Popa, V. Sasca, I. Holclajtner-Antunović, *Microporous Mesoporous Mater.* **2012**, *156*, 127.

18 I. D. Holclajtner-Antunović, A. Popa, D. V. Bajuk-Bogdanović, S. Mentus, B. M. N. Vasiljević, S. M. Uskoković-Marković, *Inorg. Chim. Acta* **2013**, *407*, 197.