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Oxidation of Some Alcohols to the Corresponding Carbonyl Derivatives Using the $H_3PW_{12}O_{40}$ HeteropolyAcid as Catalyst

Alireza Akbari[1]*, Mohammad Hakimi[1], Hassan Hassani[1], Hooshang Vahedi[1], AkramGhambari Khosh[1]

[1]Chemistry Department, Payame Noor University, 19395-4697 Tehran, I. R. of Iran.

Corres.author: a_akbari@pnu.ac.ir

Abstract: The oxidation of alcohols to the corresponding carbonyl derivatives was studied over various primarily oxidants such as H_2O_2, MnO_2, $KMnO_4$ and $K_2Cr_2O_7$ using catalytic amount of heteropoly acid, $H_3PW_{12}O_{40}$ with or without solvent. The best reaction condition for this conversion was confirmed to be solvent-free oxidation of alcohols using $KMnO_4$, catalysed by heteropolyacidkeggin [$H_3PW_{12}O_{40}$] supported by alumina.

Key Words: Catalyst; Polyoxoanione; Heteropoly acid. Novel.

Introduction and Experimental

Polyoxometalate anions have over recent years been investigated as oxidation catalysts using a variety of oxidants [1]. The use of sandwich type polyoxometalates, $[WZnM_2(H_2O)_2(ZnW_9O_{34})_2]^{12-}$(M =Mn(II), Zn(II)), for catalytic oxidation of alkenes, alkenolsand alcohols with aqueous hydrogen peroxide has been reported [2-3]. Efficient H_2O_2-based oxidation systems with three kinds of polyoxometalates, $[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]^{4-}$, $[\gamma\text{-}1,2\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$, and $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ are reported [4]. The catalytic air oxidation-trimerization of alcohols reported using hetropolyacids, $H_4[PMo_{11}VO_{40}$, $H_4[SiW_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$ and $H_5[PMo_{11}VO_{40}]$, the formation of cyclotrimers of alcohols and aldol condensation products was observed [5]. Recently, the oxidation of cyclohexanol to epsilon-caprolactone with aqueous hydrogen peroxide on $H_3PW_{12}O_{40}$ and $Cs_{2.5}H_{0.5}PW_{12}O_{40}$was studied [6].Molybdo(vanado)phosphoric heteropoly acids of Keggin structure supported on oxide supports (SiO_2, TiO_2, Al_2O_3) were used as catalysts for ethane to acetic acid oxidation in the range of reaction temperature from 250 to 400 °C. Vanadium atoms introduced into Keggin structure enhanced oxidative activity of catalytic system, while vanadyl groups exchanged into cationic position diminished ethane conversion [7].

The oxidation of alcohols to carbonyl compounds is an important transformation of organic synthesis, and several methods have been explored to accomplish such a conversion [8]. These methods involve the use of expensive reagents, long reaction times, strongly acidic condition and tedious work-up procedure leading to the generation of a large amount of toxic waste. In this paper the oxidation of alcohols to the corresponding carbonyl derivatives in the presence of heteropoly acid, $H_3PW_{12}O_{40,}$ is to be presented.

All chemical regents such as alcohols, solvents and $H_3PW_{12}O_{40}$ purchased from Merck or Fluka. FT IR - 8400 Spectrophotometer, SHIMADZU; H-NMR Bruker DPX-100 or BI- 9200- BamsteadElectrotherma were used for controlling of the products.The alumina support was provided as reported [9]. Heteropolyacidkeggin [$H_3PW_{12}O_{40}$] supported by alumina was prepared by fine mixing of the heteropoly acid (0.5 gr, 0.17 mmol) and alumina powder (0.5 gr, 0.17 mmol) for further usages. Alcohol (1 mmol) was added into a round bottomed flask followed by the oxidant (2 mmol), [$H_3PW_{12}O_{40}$] (0.01 mmol) and 5 mL dichloromethane, DCM, as solvent. The mixture was stirred at room temperature by an electrical stirrer and the progress of the reaction was monitored by TLC. After good progress of the reaction (more than 95%) which can qualitatively confirm by TLC, some more oxidant (0.5 mmol) was added and the mixture was stirred for conversion of probably little remaining alcohol. The mixture was filtered, and after evaporation of the solvent, the pure product was separated by a flash column chromatography using n-hexane/ethyl acetate (5:1). The product was characterized using 2, 4- diphenyl hydrazine which produce the yellowish orange precipitate. In some cases, the products were characterized by 1H NMR and FTIR spectroscopy. The yellowish orange precipitate was recrystallized using ethanol and finally, and the yield was calculated.

Results and Discussions

The oxidation of alcohols in the presence of $H_3PW_{12}O_{40}$ was studied over various primarily oxidants such as H_2O_2, MnO_2, $KMnO_4$ and $K_2Cr_2O_7$ and the results are outlined in the Tables 1 and 2. Table 1 show the oxidation of benzyl alcohol derivatives by hydrogen peroxide as oxidant.

Another attempt was carried out on comparing the results with free solvent conditions as well as changing in oxidant, table 2.

The results of the comparison among the oxidants showed, the oxidation can be performed in the presence of potassium permanganate more efficient and the corresponding carbonyl derivatives could be obtained in higher yields in shorter reaction times. Also the results revealed that almost in every experiment the reaction happened better in the absence of solvent.

In the next attempt the solvent effect was studied using acetonitrile, chloroform or DCM. The results are summarized in the Table 3.

Table 1: The oxidation of benzyl alcohol derivatives by H_2O_2 in the presence of $H_3PW_{12}O_{40}$ at 25^0C

Alcohol	Time (h)	Yield %	Alcohol	Time (h)	Yield %
4-BBA	96	26	4-NBA	96	17
4-ClBA	96	23	3-NBA	96	15
2-ClBA	96	20			

4-BBA = 4-bromobenzyl alcohol; 4-ClBA= 4-chlorobenzyl alcohol; 2-ClBA= 2-chlorobenzyl alcohol; 4-NBA= 4-nitrobenzyl alcohol; 3-NBA= 3-nitrobenzyl alcohol.

Table 2: The oxidation of alcohols by MnO_2, $K_2Cr_2O_7$ and $KMnO_4$ in the presence of $H_3PW_{12}O_{40}$ at 25^0C

	Alcohol	Time (h)	Yield %	Time (h)	Yield %	mmol of oxidant
		Solvent free		In DCM		
MnO_2	Benzyl alcohol	7	55	7	44	3.5
	(4-methoxyphenyl)methanol	2	50	2	48	2
	1-Octanol	6	31	6	45	3.5
	Cyclohexanol	5	42	5	40	4
$K_2Cr_2O_7$	Benzyl alcohol	4	60	4	47	2.5
	(4-methoxyphenyl)methanol	2	51	2	49	2
	1-Octanol	4	65	4	58	2
	Cyclohexanol	2	44	2	38	2
$KMnO_4$	Benzyl alcohol	2	58	2.5	63	2
	(4-methoxyphenyl)methanol	6	59	6	50	2.5
	1-Octanol	5.5	75	5.5	70	2
	Cyclohexanol	4	47	4	42	2

Table 3: Solvent effect on the oxidation of alcohols by $KMnO_4$ in the presence of $H_3PW_{12}O_{40}$ at 25^0C

Alcohol	$KMnO_4$ (mmol)	Time (h)	Yield %	Solvent
Benzyl alcohol	2	1	92	Acetonitrile
(4-methoxyphenyl)methanol	2	0.5	73	Acetonitrile
1-Octanol	2	4	90	Acetonitrile
Benzyl alcohol	2	2.3	75	DCM
(4-methoxyphenyl)methanol	2.5	6	50	DCM
1-Octanol	2	4	74	DCM
Benzyl alcohol	2	2.3	72	$CHCl_3$
(4-methoxyphenyl)methanol	2.5	6.3	47	$CHCl_3$
1-Octanol	2	4	62	$CHCl_3$

Table 4: The oxidation of alcohols by alumina supported $KMnO_4$ in the presence of $H_3PW_{12}O_{40}$ at 25^0C

Alcohol	$KMnO_4$ (mmol)	Time (h)	Yield %	$KMnO_4$ (mmol)	Time (h)	Yield %
	In DCM			Solvent free		
Benzyl alcohol	2	1	58	2	1	60
(4-methoxyphenyl) methanol	2	3	66	2.5	5	80
1-Octanol	2.5	4	50	2.5	3	63
Cyclohexanol	2.5	2.5	50	2.5	2.5	50
1-phenylethanol	2	2	68	2	1	70

The most yields and least time for the oxidation were found when acetonitrile was used as solvent. This advantage could be due to the more polarity of acetonitrile than the other solvents, DCM or chloroform. The used heteropoly acid, HPA, has more solubility in polar solvents and can act as more efficient catalyst in them.

Supported HPA catalysis is important for applications because bulk HPAs have a low specific surface (1-5 $m^2 g^{-1}$). The acidity and catalytic of supported HPAs depends on the type of the carrier, the HPA loading, conditions of pre-treatment, etc. Acidic ion-exchange resin, alumina, etc., are suitable as supporters of the activity of the catalyst. Solvent-free oxidation of aromatic alcohol was carried out by KMnO4, catalysed by heteropoly acid [$H_3PW_{12}O_{40}$] supported by alumina, and the results are given in the Table 4. Alumina powder (1.0 g, 11.11 mmol) and hetropoly acid, $H_3PW_{12}O_{40}$ (0.5 g, 0.17 mmol) was placed in a mortar and ground by hand with a pestle for 20 minutes at room temperature to prepare the hetropoly acid supported by alumina and 0.1 g of this was used in the reactions.

Conclusions

The oxidation of wide variety of alcohols to the corresponding carbonyl groups was studied using catalytic amount of heteropoly acid Keggin, $H_3PW_{12}O_{40}$ by primarily oxidants such as H_2O_2, MnO_2, $KMnO_4$ and $K_2Cr_2O_7$. It was confirmed that the oxidation was potent in the presence of potassium permanganate under a solvent-free reaction conditions. Moreover, using heteropolyacidKeggin [$H_3PW_{12}O_{40}$] supported by alumina even is more effective for the conversion of alcohols to the corresponding carbonyl groups.

Acknowledgments

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References

1. Nezhadali A. andAkbarpour M., Selective oxidation of primary substituted aromatic amines to azoxy products using lacunarycatalyses,CCL 2010, 21(01) 43-46.
2. Adam W., Alsters P.L., Neumann R., Saha-Möller C.R., Sloboda-Rozner D. and Zhang R., A Highly Chemoselective, Diastereoselective, and RegioselectiveEpoxidation of Chiral Allylic Alcohols with Hydrogen Peroxide, Catalyzed by Sandwich-Type Polyoxometalates: Enhancement

of Reactivity and Control of Selectivity by the Hydroxy Group through Metal−Alcoholate Bonding, J. Org. Chem. 2003, 68, 1721-1728.

3. Maayan G., Fish R. and Neumann R., Polyfluorinated Quaternary Ammonium Salts of Polyoxometalate Anions: Fluorous Biphasic Oxidation Catalysis with and without Fluorous Solvents, Org. Lett., 2003, 5 (20), 3547-3550.
4. Mizuno N., Hikichi S., Yamaguchi K., Uchida S., Nakagawa Y., Uehara K. and Kamata K., Molecular design of selective oxidation catalyst with polyoxometalate, Catalysis Today, 2006,117, 32-36.
5. Heravi M. M., Sadjadi S., Hekmatshoar R., AbdiOskooie H., Keggin-Type Heteropolyacids-Catalyzed One Pot Oxidation-Trimerization of Alcohols into 2,4,6-Trisubstituted-1,3,5-Trioxanes, Iran. J. Chem. Chem. Eng., 2009, 28(2), 131-136.
6. Sepúlveda J., Vera C. Yori J., Badano J., Santarosa D. and Mandelli D., $H_3PW_{12}O_{40}$ (HPA), an efficient and reusable catalyst for biodiesel production related reactions. Esterification of oleic acid and etherification of glycerol, Quim. Nova*,*2011,34(4), 601-606.
7. Sopa M., Waclawheld A., Grossy M., Pijanka J. and Nowinska K., Ethane to acetic acid oxidation over supported heteropoly acids, Applied Catalysis *A:* General, 2005, 285, 119-125.
8. Javadi A., Heravi, M.M., Bamoharram F. F. and Nikpour M., One-Pot Synthesis of TetrasubstitutedImidazoles Catalyzed by Preyssler-Type Heteropoly Acid, E-Journal of Chemistry,2011, 8(2),547-552.
9. Akbari A., MSc. Thesis, FerdowsiUniversity of Mashhad, Iran, 1992.

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